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Research Triangle Inst.
Research Triangle Park, NC

Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

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Environmental Assessment of Iron Casting

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Environmental Assessment of Iron Casting

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ENVIRONMENTAL ASSESSMENT OF IRON CASTING

ABSTRACT

Sampling of ductile iron casting in green sand molds with phenolic isocyanate cores and in phenol-formaldehyde bound shell molds did not provide definitive proof that environmentally hazardous organic emission occur. Both molding systems produced the same type of major emissions, alkyl halides, carboxylic acid derivatives, amines, substituted benzenes, nitrogen heterocyclics, and fused aromatics in quantities that slightly exceed the lowest Minimum Acute Toxicity Effluent (MATE) values for the categories, but probably not for individual compounds. GC-MS analysis revealed the major fused aromatics to be naphthalene compounds. Quantitative analysis of specific PNA's showed no significant level of concern. Inorganic dust emissions are hazardous if uncontrolled because of silicon, chromium, and nickel. The dust is sufficiently high in 12 metals to render it a hazardous waste if collected as a sludge and landfilled, but leachate testing may change that categorization. Relatively high levels of Sr, Ba, Ce, Pr, and Nd in the dust indicate that inoculation smoke should be examined.

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1.0 SUMMARY

This report presents the findings of the environmental effects of iron castings in organically bound sand molds, with particular emphasis on the organic vapors produced. The purpose of the study was to investigate the potential hazards of the process from available literature, acquire new data by sampling and analysis, and draw conclusions about the environmental acceptability of the process.

The iron-castng industry ranks sixth in value added among all manufacturers, with 1,367 foundries that can cast 19 million tons of iron per year. Sand constitutes 75 percent of the solid waste produced. While the foundry now appears as a less smoky neighbor, there is still concern for the invisible organic vapor emissions that are the result of using organic binders and additives in the sand molds. The works of Bates and Sott revealed the presence of benzo(a) pyrene and other substances of concern to human health in the emissions from iron casting.

The present study began with a review of the chemical literature to determine the possible chemical products from the pyrolysis of the organic substances used in foundry molds. This listing indicated that phenolic-isocyanate and green sand with seacoal have the highest pollution potential of the commonly used substances. Previous studies indicated that half or more of the pouring-to-shakeout emissions occur in the shakeout; therefore, this operation was selected for sampling.

Three sites were sampled:

1) A duct drawing air from the shakeout of green sand and phenolic-isocyanate core molding.
2) The exhaust stack from the wet scrubber downstream of the previous site
3) Fugitive emissions in the shakeout room of a phenolic-shell molding foundry.

The samples were analyzed using methodologies based on the Environmental Protection Agency's Level 1 protocols. Indications of possible carcinogenic material triggered a quantitative analysis by gas chromatography-mass spectrometry for a standard list of PNA compounds. The dust collected was analyzed for all the elements by spark source mass spectrometry.

1.1 PARTICULATE ANALYSIS

The results of particulate analysis were found to be:

	Before scrubbing	After scrubbing
<1 μm dust	19.2 g/tonne cast (17.4 g/ton)	19.8 g/tonne cast (18.0 g/ton)
1-3 μm dust	213.6 g/tonne cast (193.9 g/ton)	23.6 g/tonne cast (21.4 g/ton)
3-10 μm dust	863.5 g/tonne cast (783.9 g/ton)	(unmeasurable)
> 10 μm dust	5.874 kg/tonne cast (5.333 kg/ton)	(unmeasurable)
Total, including probe rinse	7.017 kg/tonne cast (6.37 kg/ton)	43.4 g/tonne cast (39.4 g/ton)

Thus, using a wet scrubber, better than 99 percent control is obtained for total particulates.

1.2 ORGANIC ANALYSIS

The total organic emissions from the shakeout of green sand molds prior to wet scrubbing was found to be 99.5 percent in the vapor state with the remainder concentrated on the larger particulates, divided as follows:

On 0-3 μm dust : not measurable

On 3-10 μm dust : 0.42 g/tonne cast
(0.38 g/ton)

On >10 μm dust : 1.32 g/tonne cast
(1.2 g/ton)

In air : 610 g/tonne cast
(554 g/ton)

Cyanide in air : 7.13 g/tonne cast
(6.47 g/ton)

The cyanide concentration was 1.68 vppm, considerably less than the MATE value of 10 vpmm.

The MATE is the Minimum Acute Toxicity of Effluent and is the concentration level at which undesirable environmental or health effects become apparent.

The organic emissions found in the shakeout emissions were tentatively identified and quantified by IR spectrophotometry according to Level 1 protocol. This produced the following results for the unscrubbed emissions from green sand casting:

TCO, mg/m^3 : 163.8
GRAV, mg/m^3 : 9.85
Total Organics, mg/m^3 : 173.7

Category	mg/m^3	Lowest MATE for category mg/m^3	Ratio $\frac{\text{conc. found}}{\text{MATE}}$
Aliphatics	0.72	20	< 1
Alkylhalides	0.22	0.1	2.2
Substituted Benzenes	2.45	1.0	2.45
Halobenzenes	0.24	0.7	< 1
Fused aromatics	2.45	0.0001 to 230	24000
Hetero N compounds	0.56	0.1	5.6
Hetero O compounds	0.10	300	< 1
Hetero S compounds	0.10	2	< 1
Alkyl S compounds	0.06	1	< 1
Nitriles	0.01	1.8	< 1
Aldehydes, ketones	0.1	0.25	< 1
Nitroaromatics	0.01	1.3	< 1
Ethers, epoxides	0.1	16	< 1
Alcohols	0.56	10	< 1
Phenols	0.56	2	< 1
Amines	0.56	0.1	5.6
Amides	0.47	1.0	< 1
Esters	0.15	5.0	< 1
Carboxylic Acids	0.46	0.3	1.5
Sulfonic Acids	0.05	0.8	< 1

Low resolution mass spectrometry failed to confirm significant levels of alkyl halides, carboxylic acids, amines, or nitrogen heterocyclics. This leaves fused polycyclics and substituted benzenes as possible areas of concern. Of the substituted benzenes listed in the MEGs, only one of the 18 has a MATE lower than the analysis for the category, namely biphenyl. This is exceeded by a factor of 2.5 only if it is the entire constituent of that fraction, which is not probable. The other category of possible concern is that of fused polycyclics. These were quantified for a standard set of PNA's by capillary gas chromatography-mass spectrometry (GC-MS). The PNA levels tested for are well below the MATE values, specifically:

Compound	Conc. $\mu g/m^3$	Air, health MATE, $\mu g/m^3$
Naphthalene	1,484	50,000
Dibenzofuran	9.8	--
Anthracene	36.8	56,000
Phenanthrene	7.6	1,600
Fluoranthene	0.7	90,000
Pyrene	0.7	230,000
Chrysene	15.4	2,200

The GC-MS analysis produced a complete mass spectrum for each GC peak, some of which were analyzed, revealing the 36 compounds that composed 79 percent of the material. The compounds identified in the ventilating air from the green sand shakeout are listed in the table on the following page. It is notable that the majority of the compounds are one- and two-ring compounds, and only one three-ring polycyclic, anthracene, was found. This indicates a trend toward minimal quantities of large polycyclic compounds. In summarizing the organic analysis, the level 1 procedure provides no definitive evidence that the substances present exceed their MATE values in the shakeout effluent

Chromatographic peak no.	Relative peak height	Percent of sample	Compound
1	.34	4.2	Aniline
2	.18	2.2	Phenol
3	.14	1.7	Cresol isomer
4	.49	6.0	$C_{11}H_{24}$ isomer
5	.11	1.3	Naphthalene
6	.18	2.2	C_5-alkylbenzene isomer $C_{12}H_{26}$ isomer
7	.12	1.4	Dimethylindan isomer
8	.12	1.5	Dimethylindan isomer C_6 alkylbenzene isomer
9	.19	2.4	C_6 alkylbenzene isomer $C_{14}H_{30}$ isomer Dimethylindan isomer
10	1.00	12.3	β-methylnaphthalene Unsaturated C_6 alkylbenzene isomer C_6 alkylbenzene isomer
11	.73	9.1	$C_{13}H_{28}$ isomer α-methylnaphthalene
12	.28	3.5	Ethylnapthalene isomer Trimethylindan isomer
13	.68	8.3	Ethylnaphthalene isomer $C_{14}H_{30}$ isomer
14	.59	7.2	Dimethylnaphthalene isomer Diphenylmethane
15	.34	4.2	Dimethylnaphthalene isomer
16	.18	2.2	Dimethylnaphthalene isomer
17	.21	2.6	$C_{15}H_{32}$ isomer C_3 alkylnaphthalene isomer
18	.13	1.6	C_3 alkylnaphthalene isomer
19	.14	1.7	C_3 alkylnaphthalene isomer
20	.15	1.8	$C_{16}H_{34}$ isomer Di-p-tolymethane (tent.)
21	.11	1.3	$C_{17}H$ isomer Anthracene-d_{10}

from green sand molding in a well-ventilated foundry. The results can be viewed as borderline because some categories have concentrations equal or slightly greater than the lowest MATE in the category, but the large number of compounds reduces the probability that any specific compound is present above its MATE level. This indicates that Level 2 analysis is required to determine if the pollutant levels are above the MATE levels. The analytical results did indicate, as discussed later, that the pouring process is a more probable source of high molecular weight polycyclic compounds and should be given higher priority than the shakeout in future investigations.

1.3 INORGANIC ANALYSIS

The respirable portion of the particulate (<3μm) was subjected to spark source mass spectrometry. Aluminum, magnesium, and silicone dominated the analysis, which is consistent with the major composition of the dust being clay and silica. The analysis shows quantities of Si, Cr, and Ni, in the unscrubbed shakeout emissions greater than the air, health MATE values. The worst case, Cr, can be held within the MATE level by 98.6 percent removal of all particulates; however, only 25 percent of the < 1 μm particulates are removed by the wet scrubber. Assuming the total particulates from the scrubber have the same analysis as the < 3 μm particulates that were analyzed, the following results were computed:

Total scrubber exhaust particulates: 8.92 mg/m^3
Cr concentration: 1100 μg/g particulate
Cr emission: 9.8 μg/m^3
Cr air, health MATE: 1 μg/m^3
TLV: 100 μg/m^3.

The TLV or Threshold Limit Value is the level of contaminants considered safe for the workroom atmosphere, as established by the American Conference of Governmental Industrial Hygienists (ACGIH). Ten hours per day or 40 hours per week exposure is assumed.[91]

This shows that while chromium is safe by TLV standards, it exceeds the MATE standards, thus it is difficult to definitively assess the situation. Although small amounts of chromium is sometimes added to the metal, there was not an identifiable source of chromium at the time of testing. The presence of impurities in the selected scrap used is always a possibility.

An unexpected finding of the inorganic analysis was the presence of Zr, Ba, La, Ce, Pr, and Nd at levels above a background of other metals not normally a part of the system (i.e., Zr-140 ppm; Ba-150 ppm; La-28 ppm; Ce-100 ppm; Pr-4.7 ppm; Nd-17 ppm). These are additives to the magnesium inoculation alloy and were not expected to show up at the shakeout. This indicates that the nature of the inoculation smoke should be examined more closely.

2.0 CONCLUSIONS

This study was a Level 1 assessment which indicated that most emissions were less than MATE values but some may exceed MATE values, although there is no definitive proof that is the case. Several areas of concern were identified, however, such as:

1. Chromium emissions after scrubbing exceed the MATE value although they are well under the TLV. The source of the chromium could not be determined.
2. If the sludge from the wet scrubbers is landfilled it may be classified as hazardous in Ca, Ti, Cr, Mn, Ni, Cu, Zn, As, Se, Cd, and Pb, based on particulate analysis. Leach testing will have to be performed to determine if the sludge is unacceptable for landfilling under RCRA.
3. The shakeout particulates contained notable amounts of Zr, Ba, Ce, Pr, and Nd. These are common additives to magnesium inoculation alloys. The inoculation smoke can be expected to contain much higher concentrations of these elements.
4. If the shakeout emissions are not collected and scrubbed or otherwise subjected to pollution control processes, the emissions of silicon, nickel and chromium exceed the health MATE values.
5. Positive identification of carcinogens in notable quantities will require level 2 testing. The results of the present study indicate that the pouring and early cooling stages are more probable sources than the shakeout.
6. The emissions from the shakeout are a function of the metal temperature at the time of shakeout, according to a theoretical model derived in this report. This signals an additional parameter to be monitored if emissions are monitored, and a possible way of controlling emissions.

3.0 INTRODUCTION

The foundry industry is basic to an industrial society. Since the 19th century it has been an important producer of farm implements, water pipe, and valves. In this century, all power-producing machines, electric motors, internal combustion engines, and steam turbines are made by the foundries from castings. Most of these castings are made in sand molds that either contain organic additives (for casting purposes) or are bound together by organic polymers. Over 220 million pounds of organic polymers were used by the foundry industry in 1971, and their use is increasing because of the better castings obtained.

The organic additives and binders used in iron casting decompose under the heat of molten iron to produce smoke and vapors of unknown composition. These were studied in the laboratory by Bates and Scott[21] who collected the emissions and subjected them to partial analysis. Their work identified benzo(a)pyrene but quantities were not reported.

The objective of this study was to determine if potentially hazardous organic materials are generated by pyrolysis of mold materials used in iron casting. The problem of smoke on particulate emissions from foundries has been reduced by the employment of air pollution control devices, namely wet scrubbers and baghouses. While foundries were now visually cleaner, the organic vapor emission levels were unknown and needed determination. Although the initial interest was the organic emissions, following Level 1 protocol resulted in important discoveries about inorganic particulate emissions.

4.0 INDUSTRY DESCRIPTION

In 1976 there were 4,517 foundries in the United States.[1] Of these 1,367 were iron foundries (Table 1).[2] Over the past decade the industry has shown a trend toward fewer but larger foundries with an average annual attrition rate of approximately 75 plants, most of which are small, closely held operations. Today, the industry is in a state of transition from one that has been labor-intensive to one that is capital-intensive. As a result, the foundry industry now ranks sixth among all manufacturing industries based on value added by manufacture, increasing from $476 per ton in 1966 to $1,011 per ton in 1976. A density distribution of U.S. iron foundries is given in Figure 1. The highest concentration of foundries is in Pennsylvania, Ohio, Michigan, Illinois, Wisconsin, New York, and Indiana, accounting for more than half of the iron-casting capacity of the nation. Two-thirds of the iron foundries are located in metropolitan areas. The decline in foundries has taken place mostly in the smaller metropolitan areas with only a slight change in the larger areas.[4] Figure 2 gives the status of casting production in the United States from 1965 to 1977.[2] As shown on the figure, there has been an overall decline, some of which has been caused by production changes as the steel industry perfects methods of sheet metal fabrication.

The major change in the industry in the past decade has been a decline in the use of the cupola for iron melting, with an increase in the use of electric induction furnaces and electric arc furnaces. There is also a continuing trend toward automated casting lines, which adversely affects many smaller foundries. Chemically bound sand is easy to handle on automated equipment and the economic pressure to reduce cost, along with automation, is causing a continual increase in the use of chemically bound sand. Another major reason for increasing reliance on chemically bound sand is the declining availability of highly skilled labor and the fact that chemically bound sand produces a better product, even with less skilled labor.

TABLE 1. FOUNDRIES AND IRON FOUNDRIES IN EACH STATE AS OF 1976

State	Foundries	Iron Foundries	State	Foundries	Iron Foundries
Alabama	90	64	Missouri	108	26
Alaska	1	1	Montana	3	3
Arizona	19	3	Nebraska	24	8
Arkansas	43	9	Nevada	4	2
California	440	8	New Hampshire	29	8
Colorado	50	12	New Jersey	134	29
Connecticut	101	20	New Mexico	8	1
Delaware	2	1	New York	282	66
D. C.	2	1	North Carolina	57	27
Florida	60	12	North Dakota	3	2
Georgia	44	25	Ohio	465	152
Hawaii	3	2	Oklahoma	45	22
Idaho	6	4	Oregon	54	12
Illinois	333	81	Pennsylvania	386	157
Indiana	198	75	Rhode Island	57	8
Iowa	77	35	South Carolina	29	12
Kansas	57	23	South Dakota	1	1
Kentucky	30	13	Tennessee	76	40
Louisiana	24	8	Texas	175	66
Maine	16	8	Utah	19	12
Maryland	26	10	Vermont	4	4
Massachusetts	141	43	Virginia	48	29
Michigan	351	111	Washington	53	18
Minnesota	84	35	West Virginia	28	13
Mississippi	16	7	Wisconsin	200	88
			TOTAL	4,517	1,367

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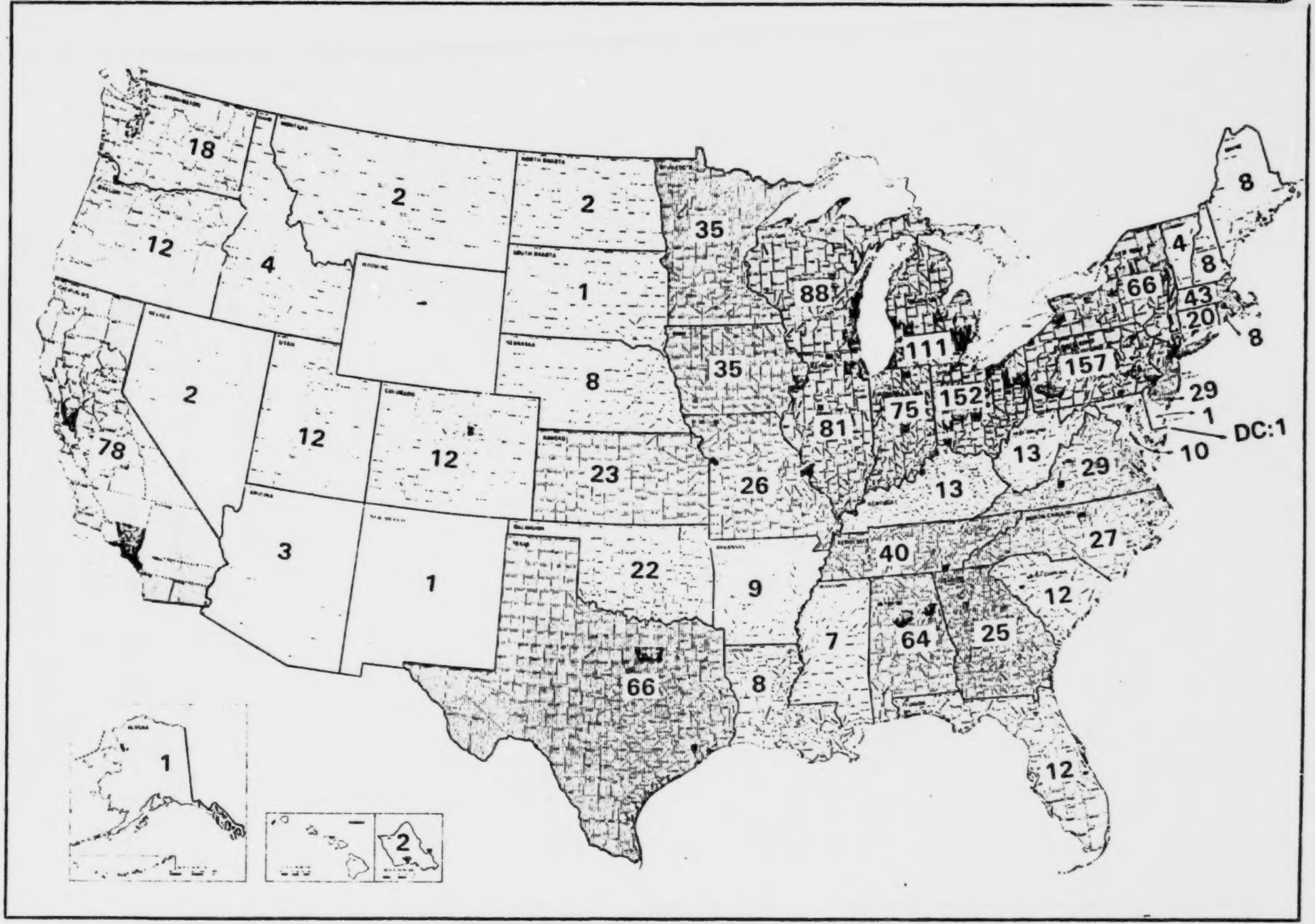

18
2
2
8
12
4
35
4
8
66
43
88
1
-
20
8
111
157
2
35
8
29
75
152
1
81
DC:1
12
12
78
23
26
13
10
13
29
27
40
3
1
22
9
12
7
64
25
66
8
1
12
2

Figure 1. 1978 density distribution of iron foundries.

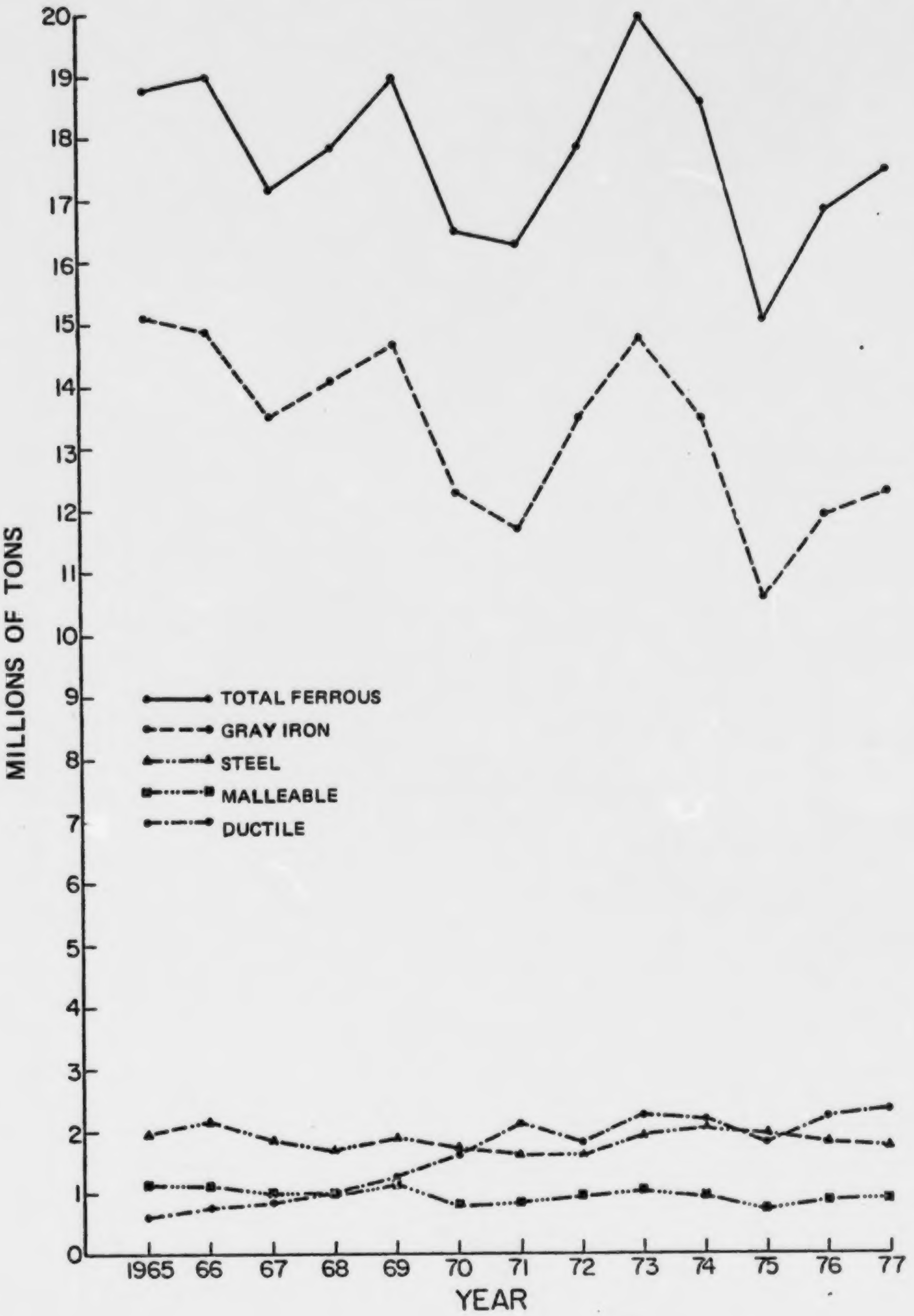


FIGURE 2. Casting production in the U.S.

5.0 PROCESS ANALYSIS

The methods of sand casting used by foundries today are sophisticated compared to those of 50 years ago. Nevertheless, the principal processes remain the same. A model is made of wood, metal, or plastic, and placed in a container, which is then packed with sand. Clay and other substances are added to increase the shape-holding ability of the sand. After this, the model is removed and molten metal is poured into the cavity and allowed to cool. Once cool, the mold is broken and discarded leaving a cast iron copy of the desired object.

Upon cooling from the molten state, cast iron (iron containing 3 to 5 percent carbon) can form seven basic metallurgical structures. Five of these structures result from the plain metal containing sulfur impurities and the other two result from desulfurized metal. Ordinary cast iron, containing sulfur impurities and frequently silicon and manganese, forms white, pearlitic gray, or ferretic gray cast iron according to the rate of cooling. The white cast iron can be further transformed into either pearlitic, or ferritic malleable forms by heat treatment. If the hot metal is desulfurized, either pearlitic ductile, or ferritic ductile cast iron is formed according to cooling rate. The outstanding characteristic of the "ordinary" gray cast iron is the presence of graphite in the form of carbon flakes that causes the metal to exhibit brittleness. Graphite is also present in the malleable and ductile cast irons but in the form of spherical nodules. In addition to the types of cast iron previously discussed, hybrid forms are often created for special purposes by varying the cooling rates involved, sometimes by oil quenching.

Figures 3 and 4 present a flow sheet and a graphic presentation of the major operations and equipment involved in the foundry industry.[1,4]

5.1 CASTING METHODS

There are two basic casting methods utilized by the foundry industry. One is to pour the molten metal into the mold and the other is pressure

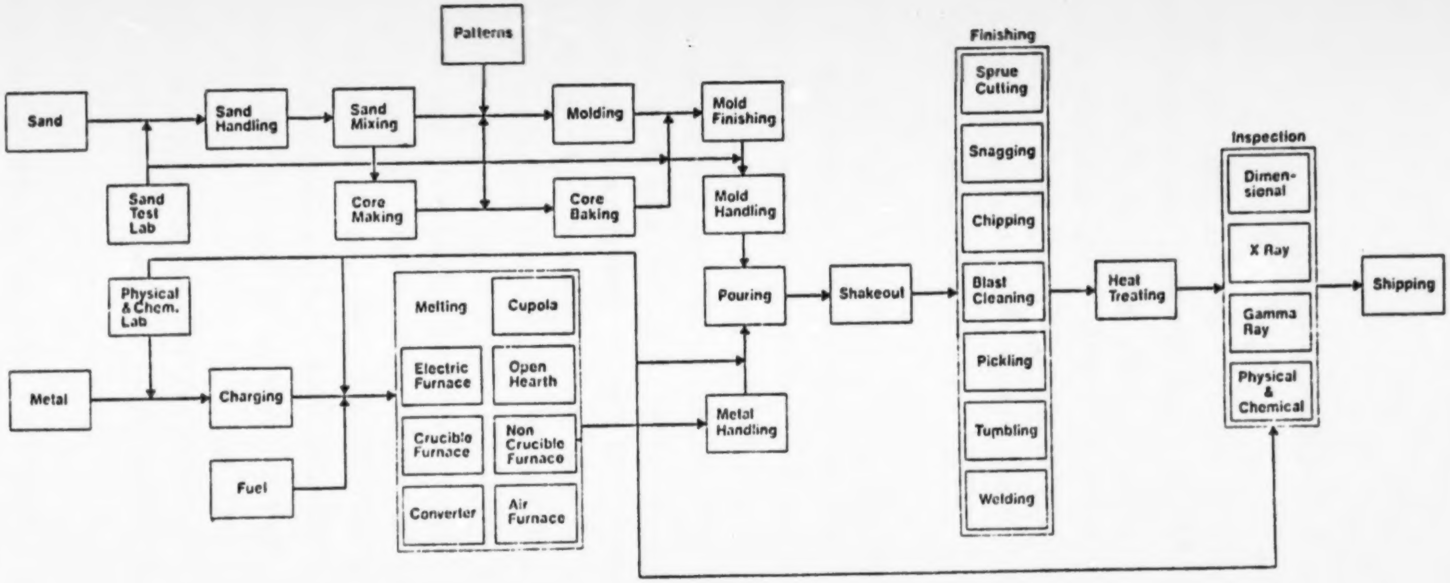

Sand
Sand Handling
Sand Mixing
Patterns
Molding
Mold Finishing
Sand Test Lab
Core Making
Core Baking
Mold Handling
Physical & Chem. Lab
Metal
Charging
Fuel
Melting
Cupola
Electric Furnace
Open Hearth
Crucible Furnace
Non Crucible Furnace
Converter
Air Furnace
Pouring
Metal Handling
Shakeout
Finishing
Sprue Cutting
Snagging
Chipping
Blast Cleaning
Pickling
Tumbling
Welding
Heat Treating
Inspection
Dimen-sional
X Ray
Gamma Ray
Physical & Chemical
Shipping

Figure 3. Typical Foundry production flow chart.[1]

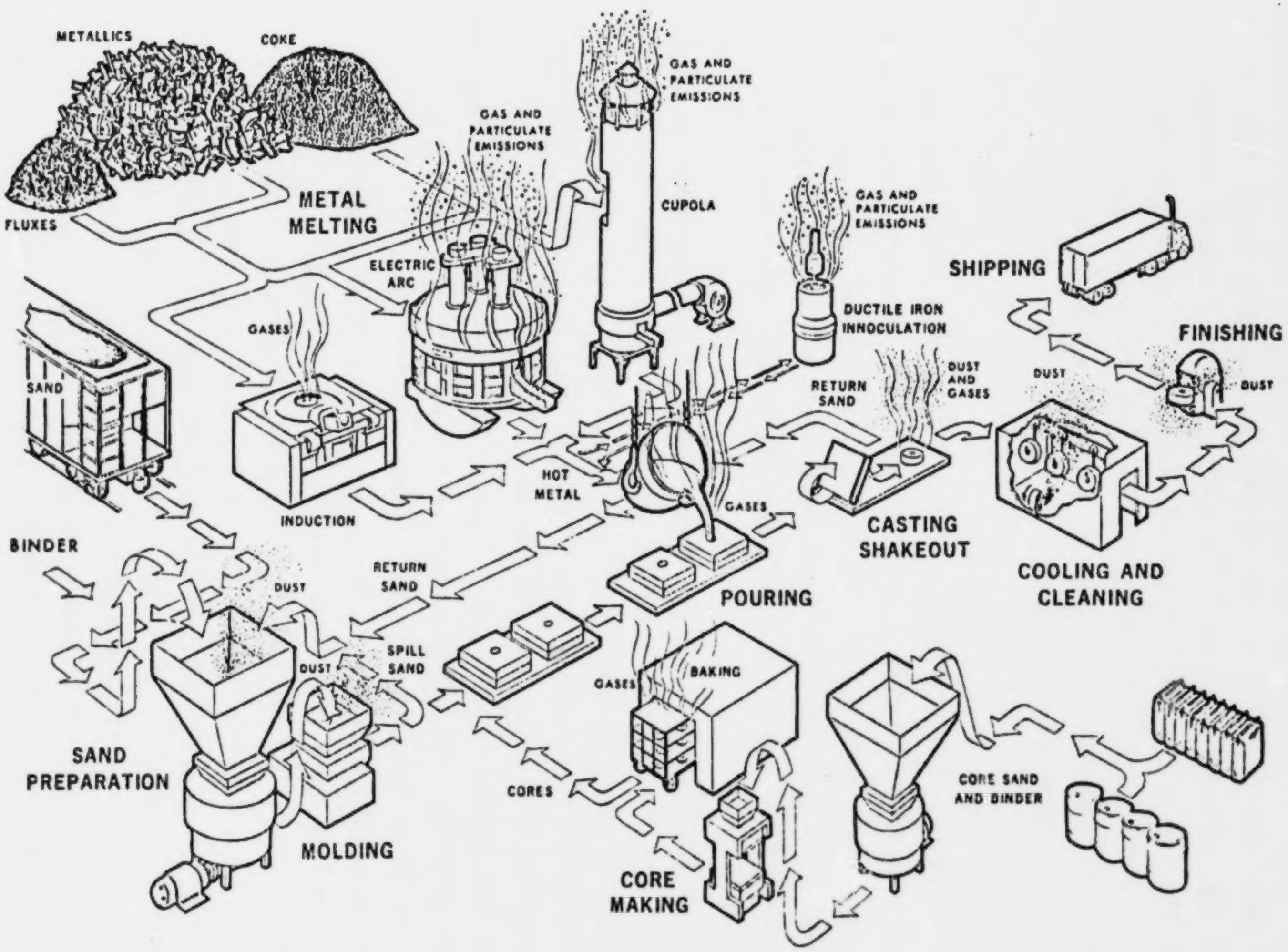

METALLICS
COKE
FLUXES
METAL MELTING
GAS AND PARTICULATE EMISSIONS
GAS AND PARTICULATE EMISSIONS
CUPOLA
ELECTRIC ARC
GAS AND PARTICULATE EMISSIONS
DUCTILE IRON INNOCULATION
SHIPPING
FINISHING
DUST
SAND
GASES
INDUCTION
HOT METAL
RETURN SAND
DUST AND GASES
DUST
GASES
CASTING SHAKEOUT
COOLING AND CLEANING
BINDER
DUST
RETURN SAND
POURING
DUST
SPILL SAND
GASES
BAKING
SAND PREPARATION
CORES
CORE SAND AND BINDER
MOLDING
CORE MAKING

Figure 4. Iron Foundry process flowsheet, emission sources.[4]

injection of the metal, usually by throwing it into the mold on a centrifuge. However, the industry refers to casting methods according to the type of mold used and, sometimes, according to the type of mold binder utilized. This results in a large number of so-called methods. The methods that will be discussed herein are (1) green sand, (2) inorganic bound sand, (3) organic bound sand, (4) permanent molds, and (5) physically bonded molds (sometimes called the third generation method).

5.1.1 Green Sand

Green sand is the original mold type and is still the predominant material in the foundry industry today. Originally, naturally binding sands or pure silica sand with desirable grain size, shape, and flow properties were employed with the addition of clay and water as a binder. Later it was learned that the addition of organic materials to the sand improved the casting quality.

The term "green sand" is applied when the chief bonding agent is clay, usually western or southern bentonite (montmorillonite). The clay is plasticized with about 3 to 5 percent water and organic materials such as sea coal, wood flour, oat hulls, and substances that are the "pot ends" of organic chemical production are added in amounts up to 8 percent. The purpose of the organic addition is to cushion the thermal expansion, provide a reducing atmoshere, and promote graphite formation at the sand-metal interface to give a better finish to the metal.

Once the pattern or blank is fabricated half of it is placed in the bottom (called the drag) of a flask and the green sand mixture is packed around and on top of the pattern either by hand or hydraulic press. In similar fashion, the other half of the blank is placed in another flask (called the cope), filled, and then the drag and cope are put together as a complete mold[5] (Figure 5). In modern foundries, machines make up the cope and drag simultaneously at a rate of about one every ten seconds and hydraulic pressure is applied through a large number of small metal feet to compress the sand into the mold. A major disadvantage to this mold is that, although it can withstand the casting process, it is easily damaged.

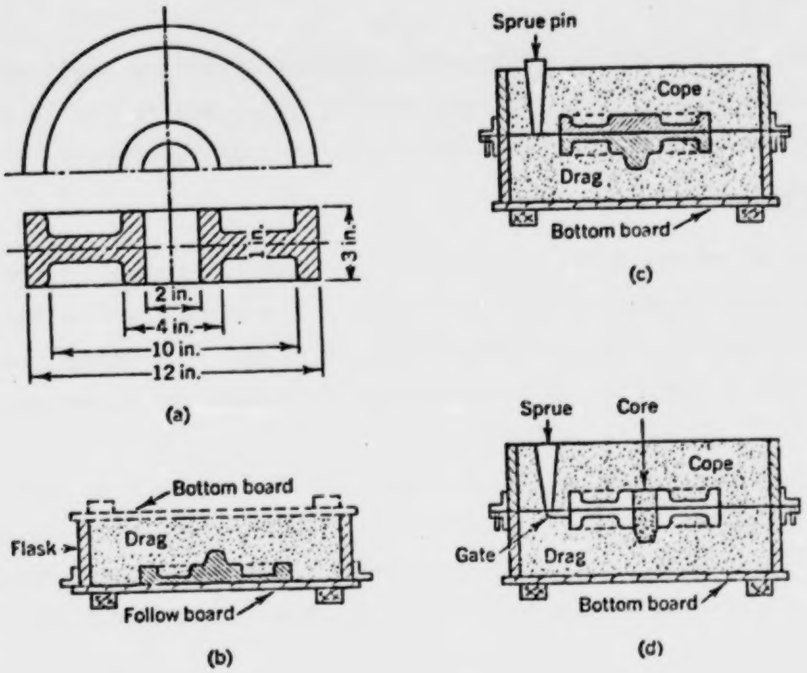

Sprue pin
Cope
Drag
Bottom board
(c)
3 in.
1 in.
2 in.
4 in.
10 in.
12 in.
(a)
Sprue
Core
Cope
Gate
Drag
Bottom board
(d)
Bottom board
Flask
Drag
Follow board
(b)

Figure 5. Typical green sand mold, (a) machined blank, (b) drag, (c) cope, (d) finished mold.

5.1.2 Inorganically Bound Molds

There are foundries that use plaster of paris, sand and plaster of paris, or a form of portland cement mixed with sand to create this small mold category. The molds that are produced make very high quality castings, but the manufacturing time involved makes them expensive and, therefore, limited to speciality work.

The most promising type of inorganic binder in present use is sodium silicate. When this material is mixed with sand, a solid gel is formed as carbon dioxide gas is blown through the mold. Mold formation is identical to the green sand process and is virtually nonpolluting.[8] However, technical difficulties are involved with the binders because they are too strong and do not weaken from hot metal addition. Therefore, removal of the mold from the metal can be difficult.

5.1.3 Organically Bound Sand

The availability of synthetic resin organic binders has resulted in a large number of mold making techniques, some of which are shell molding, hot box molds, cold set binders, no bake resins, oils, and full mold process. Table 2 presents a listing of the more popular organic binders.

Shell Molding

In this technique a mold, about 3/4 in. thick, is made in two pieces which are clamped together forming a shell. Since the shell alone would not withstand the weight of the molten metal, it is set in a large flask (typically a small railcar) and surrounded with iron shot for added support before the iron is poured into it.

Shell molding is used for high precision casting such as small engine parts. An advantage to this type of mold is that it promotes faster metal cooling, which is metallurgically desirable. Nearly all shell molds are made from phenol-formaldehyde which requires baking for about one minute.

TABLE 2. ORGANIC CORE BINDERS

- OILS
  - Core oils (oven-baked)
  - Oil-oxygen (no-bake)
- URETHANES
  - Alkyd isocyanate (no-bake)
  - Phenolic isocyanate
    - a. Gassed
    - b. Ungassed (no-bake)
- HOT BOX (heated core box)
  - Urea-formaldehyde
  - Phenol-formaldehyde
    - a. Novalak
    - b. Resole
  - Furan
  - Modified
    - a. Urea-formaldehyde/furfuryl alcohol (UF/FA)
    - b. Phenol-formaldehyde/furfuryl alcohol (PF/FA)
    - c. Phenol-formaldehyde/urea-formaldehyde (FF/UF)
- ACID NO-BAKES
  - Furan
  - Phenol-formaldehyde

Hot Box Molds

These molds are fabricated of sand bound with thermosetting resins such as phenol-formaldehyde, and require baking to set the resin. Using this definition, shell molds may also be categorized as hot box if phenol-formaldehyde is used as the binder. Other modifications such as urea-formaldehyde, furan, and phenol-formaldehyde/furfuryl alcohol resins are used for hot box molds. These resins are well established as heat stable polymers that do not soften, but under extreme temperatures, do degrade and weaken, the ideal characteristic for a sand binder.

In recent years, however, these molds have become unpopular because of the time and energy consumption required, the high equipment cost, and also cold set binders have been found to be time and energy efficient. In some cases, however, these disadvantages are outweighed because of the strength of the cores produced by this method. For example, the automotive industry has found an actual cost reduction and production increase of intricate, fragile water jacket cores by using furfuryl-phenolic resins and hot box technique.[9]

Cold Set Binders

Cold set binders, developed about 1967, are urethane resins hardened by passing a catalyst gas (triethylamine (TEA) or dimethyl ethylamine (DMEA)) through the mold. The mold itself is actually made of two resins, a phenolic resin and a polyisocyanate mixture which is incorporated with the sand. The mold making machine clamps together two metal molds shaped so as to cast the sand mold or core desired, and the sand mixture is blown into the mold by a pneumatic process. The catalyst gas is then blown through the mold and the resins harden in about 3 to 15 seconds depending on size. The metal molds then separate and the sand mold is ejected from the machine.[10] This system is used almost exclusively for core making.

No-Bake Resins

No-bake resins are polymer systems which are catalyzed while mixing with the sand and harden over a relatively short period of time but sufficiently long to enable the sand to be packed into a pattern to make a mold. The materials used for this process can be either certain urethane or certain phenol-formaldehyde resins. The earliest no-bakes were drying oils.

Oils

Oils were the earliest form of chemical binder. Core oils were various oil mixtures that hardened when baked. The drying oils, such as linseed and tung oil, that are used in no-bake operations are oils that react with oxygen in the atmosphere and harden. While similar to varnish in composition, these contained large amounts of lead and cobalt drying catalyst.

Full Mold Process

In the full mold process, the pattern is made of styrofoam using a standard plastic molding machine. The metal molds are clamped together, styrofoam beads are poured into the mold, and steam is blown through which causes the beads to expand and fuse together forming a solid block in the shape of the cavity. The styrofoam is placed in a flask and either organically bound or physically bonded sand is packed around it. The completed mold is sent to the pouring station where the molten metal is poured directly on top of the styrofoam. The styrofoam either vaporizes or turns to graphite, which promotes a fine finish, and the metal comes to rest in the sand mold.[12,17]

5.1.4 Permanent Molds

From an environmental viewpoint, permanent molds are the ultimate casting method since there is no pollution involved. In this system, the mold is made of steel, cast iron, or ceramic and, therefore, there are no substances to decompose under the heat of the metal. The disadvantages to this system, however, are that they are expensive and time consuming.[21]

5.1.5 Physically Bonded Molds

This is the newest casting method and holds the greatest promise for low environmental effects in the future. Physically bonded molds are molds in which sand is not bound together chemically.[14] Also in this method sand is not always used; powdered iron can be used instead. An example of this type of mold process is the ice bonded mold which is used by a company in England.[15] Wet sand is packed around the pattern halves in the cope and drag, placed in a freezer and frozen. The mold halves are then removed, assembled, and cast iron poured in. It results in no pollution since after the metal is removed, the moist sand which remains can be reclaimed. From an environmental viewpoint, this system is ideal; however, currently there is little application beyond a few users. Perhaps its unorthodox nature and the freezing time required are inhibiting factors. It appeared that this method more readily lends itself to a small foundry rather than a large, high production facility, assuming that a practical rapid freeze method cannot be found.

The term "physically bonded molds" is becoming synonymous with the term "third generation molds" and includes molds in which the sand is held in position by air pressure, or powdered iron is used in place of sand and frozen into position by a magnetic field. In both of these processes, a styrofoam pattern is made, placed in a flask, and surrounded by sand or granular iron. In the magnetic process, the flask is placed in a magnetic field, bonding the iron particles together, and the hot metal is poured on top of the styrofoam, vaporizing it. After the metal has cooled, the magnetic field is turned off and the cast object is removed. In the sand process, after the sand is placed around the styrofoam pattern in the flask, it is stabilized by applying a vacuum through vents on the bottom of the flask pulling the sand down and packing it tightly.[14] Another variation utilizes a layer of plastic over the top of the mold giving maximum pressure from the atmosphere against the sand.

There is also another third generation process called the "V" molding process.[18,19] In this, a sheet of ethylene vinyl acetate 0.002 in. thick, is heated to its softening point and vacuum molded around the pattern. Sand is placed on top of this and another sheet of plastic is laid over the top of the flask. A vacuum is applied to the flask through side vents attracting the two sheets of plastic and compressing and binding the sand. The flask and mold are removed from the pattern, the two halves are assembled, and casting proceeds under vacuum. After the metal is cooled, the vacuum is released and the sand is fluidized and poured out of the mold.

These processes involve no chemical binders and are relatively pollution free. Although a small amount of polymer material is vaporized, the nature and quantity is such that the pollutants expected from them is minor compared with the chemically bonded molds. It has been proposed that either magnetic or vacuum molding processes can be utilized for any of the desired molding problems within the foundry industry with a few exceptions. Because of the low capital investment, low pollution involved, and the potential for high speed production, these practices are recommended for the future.

5.2 SUPPORTING PROCESSES

5.2.1 Pattern Making

As stated previously, all molds are made from patterns of almost any material. However, most often the material used is aluminum because it is easy to fabricate and handle, lightweight, and wears well. Sometimes the aluminum patterns are nickel plated to further increase their wear resistance. All foundries have a small group employed in pattern making, the environmental aspects of which are similar to a woodworking or metal working shop.

5.2.2 Sand Processing

Previously, when naturally bonded molding sand was universally used for green sand molding, the only preparation required was the addition of water to the sand along with some make-up sand. However, reliance on a naturally occurring product of highly variable properties does not allow for high production of precision parts and, therefore, modern foundries no longer utilize naturally bonded sand. Today, the sand is mixed to order according to the recipe of the caster. Pure, clean silica sand is sized and mixed with the desired quantities of specific types of clay, water, binders, and additives in a device called a sand muller and then conveyed to the molding units. After the molding is completed, the sand is cooled and recycled. Lumps, pieces of iron, and other debris are screened out, and the sand is screened to the desired size range. The reclaimed sand is analyzed and make-up sand plus other additives are introduced according to chemical and physical analysis. Then the sand is ready for reuse. In a typical large foundry about 20 percent of the sand is replaced with new sand each day. The build-up of carbonaceous materials as well as the production of fines and other mechanical degradation prevent continual reuse of the sand.

5.2.3 Iron Melting

There are three major methods of iron melting for foundry use--the cupola, the electric induction furnace, and the electric arc furnace (EAF). There are other methods most of which involve the reverberatory furnace. However, this furnace constitutes less than two percent of the industry although it merits environmentally because of its low particulate emissions.

Cupola

The cupola is a vertical furnace having the appearance of a miniature blast furnace but distinctly different. The number of cupolas in the United States is declining despite some claims of economic advantage over the electric furnaces. The reasons given by foundries for this decline is the pollution problem and greater operational ease of the EAF and induction furnace.

In the cupola, scrap metal and coke are top loaded into the furnace and blasts of air from the bottom burn the coke and melt the metal. Fluxing material is also added, producing a slag. The conventional cupolas are made of sheet metal and lined with refractory brick; a water-cooled cupola is lined with carbon blocks and has a continual flow of water covering the outside. The cupola is operated with a blast of hot air at the bottom similar to the blast furnace and is amenable to many different techniques for controlling the manner, temperature, and position of the air emission. There are some instances of successful operation with natural gas injection, as well as utilization of pure oxygen which has the advantage of reducing stack gas volume. Because the cupola is charged through a hole in its side, the manner of operation of the doors in the charging hole determines whether or not air is mixed with the offgases. If the charging door is open continuously, large amounts of air infiltrate, increasing the volume of gas to be handled by the air pollution control system. On the other hand, if the door is closed, insufficient air is introduced to complete combustion of the carbon monoxide in the offgas. In this case, a common practice is to deliberately add adequate air and install an after-burner above the charging hole to insure the ignition of the carbon monoxide laden offgas.

A typical cupola producing medium strength cast iron from a cold charge will utilize the following quantities of material: (as percentage of iron input) scrap steel - 42 percent; foundry returns - 58 percent; FeSi - 1.1 percent; FeMn - 0.2 percent; total coke - 14 percent, limestone - 3 percent; and melting loss - 2 percent. In addition, the following materials are used in operation:[7]

Refractories, cupola	3.3 kg/metric ton
Refractories, slag skimmer	2.2 kg/metric ton
Cooling water	1.2 m^3/metric ton
Water for slag/granulation	0.11 m^3/metric ton
Fuel for preheating	2.2 kg/metric ton

As with the blast furnace, the cupola is under continual development. Coke consumption can be as high as 352 pounds per ton but with hot blast design, this can be reduced to 150 pounds per ton. Cokeless cupolas have been designed but are not in common use. Supplementary hydrocarbons and oxygen enrichment are also under research and development, as well as systems for recovering the heat from the cupola and utilizing it to heat the entire factory.

Induction Furnaces

The simplest induction furnace is a cylindrical or cup-shaped vessel lined with a refractory material and with water-cooled electrical wires around its circumference. The coil of wire is energized with an alternating current and the magnetic field set up by this process causes the metal in the furnace to reach melting temperature. When the metal has melted, the magnetic fields generated by the exciting coil interact with magnetic fields generated within the metal by the circulating current. This results in the metal undergoing a strong stirring action. This type of furnace is referred to as a coreless furnace because it contains only an electrical coil wrapped around a cylindrical container.

The channel induction furnace differs from the coreless furnace in that a tube, positioned above the bottom, passes horizontally through the furnace. Within this tube there is an iron core wound with wire. The core extends outside the furnace and loops back making connection with itself. The channel furnace requires that a continuous circuit of iron or metal exists around this core within the furnace, and only the iron in the lower portion of the furnace immediately surrounding the channel is heated. Some residual metal must always be left in the furnace for it to operate.

Induction furnaces are best suited for batch type operations although some have been recently designed for continuous operation. The coreless type is better adapted for melting whereas the channel type is better suited for holding or superheating metal. These furnaces operate at frequencies of 60 and 180 and sometimes up to 1,000 cycles per second. Generally only the very small furnaces operate at high frequency. Laboratory furnaces of a few ounces capacity require radio frequency current but the frequency can be reduced as the size of the furnace increases. Most industrial sized furnaces operated on 180 or 60 cycles.

The induction furnaces are very efficient, exhibiting very low melting losses and very high recovery of alloy additions. They are usually charged with scrap steel and cast iron scrap, foundry returns, and ferrosilicon and carbon according to the compositional requirements. If channel furnaces or furnaces containing molten metal are being charged, the charge is dried so as to prevent explosions that would occur if wet metal was charged into molten metal. No chemical actions take place in the furnace, so it is not a refining furnace. After the metal has melted, additions of pelletized coke are made to adjust the carbon content. Because it is not a refining furnace, great care must be taken to control the composition of the scrap metal charged into it to prevent metal contamination. The major pollution problems that can occur from induction furnaces are those that would result from the charging of dirty and oily scrap metal. This can be obviated with a hood system over the furnace which then traps the emissions in a fabric filter system.

Electric Arc Furnaces

The EAF is considerably different from other types of electrical furnaces both in operating characteristics and in environmental concerns. The furnace consist of a refractory lined, cup-shaped steel shell with a refractory lined roof through which three graphite electrodes are inserted. As used in iron foundries, the holding capacities vary from about 500 pounds to 65 tons, with 25 tons being more common size. The roof of the furnace is removable to allow charging and pouring. The furnace is usually charged with a bottom dump bucket. The roof is replaced and three electrodes, connected to a system of transformers fed by 3-phase alternating current, are lowered into the metal. Upon contact, there is a short period of time during which the electrodes are arcing to various pieces of scrap metal. Soon a smooth electrical discharge is formed between the electrode and metal and the melting proceeds smoothly. The distance between the electrodes and the metal, the voltage, and current parameters are continuously adjusted to maintain an optimum electrical arc. This arc is a plasma in which reactions take place, virtually all of which produce air emissions. Iron oxide is produced and, if zinc is present in the scrap, a zinc ferrite is likewise produced. The oxides formed in the electrical arc tend to be of the ferrite structure. At the present time it is normal practice for an air pollution control system to be utilized with EAFs to capture and filter (baghouses) the dust produced. When the metal has melted, the carbon content is adjusted by the addition of petroleum coke or other carbon material. When the metal is at the desired temperature and composition, the electrodes are raised out of the furnace and the entire furnace is tilted to pour the metal from it. It is common practice to add a small amount of calcium carbonate to act as a flux.

5.2.4 Inoculation

Inoculation is the process of introducing certain alloying elements into the iron thereby causing the graphite in the iron to form spheroidal particles resulting in ductile iron. No other metal alloy has had as rapid an increase in production as ductile iron. Shipments of ductile iron castings increased from 200,000 tons in 1963 to 2,200,000 tons in 1973. The increased emphasis of high strength to weight ratio in the automative industry is a major factor in this growth.[88]

Ductile iron is based on innoculation with magnesium but other elements such as Ba, Ca, Ce, Nd, Pr, Sr, and Zr are also added. The magnesium may be added as a wire or block submerged in the molten iron, but increasingly the practice is to use ferrosilicon alloys containing the magnesium, or porous blocks of steel turnings impregnated with magnesium. The final cast iron must have 0.035 percent Mg for the alloying to be effective, but 0.04 to 0.8 percent is added, depending on the chemistry of the metal and the operational nature of the foundry, because of fading. (Since the melting point of iron is above the boiling point of magnesium, the magnesium added to the iron is lost in a short period of time. This phenomenon is called fading.) The effectiveness of inoculation (retained magnesium) fades 50 percent every five minutes after magnesium introduction until the metal has cooled substantially.[89]

A common method of innoculation is to load the magnesium or magnesium containing ferrosilicon into a graphite "bell". The bell contains holes and a rod is placed across the bottom to retain a container of inoculant. This bell, mounted at the bottom of a vertical graphite rod is then plunged deep into a ladle of molten iron. A turbulent reaction ensues because the magnesium boils under the heat of molten iron. As much as 65 percent of the magnesium may be lost in this process, and the Mg vapor that issues from the iron ignites in air, creating large quantities of smoke.[4] This is presumed to be MgO, but many other possibilities exist, as will be discussed below. Numerous methods of inoculation have been tried, and the problem of efficiently accomplishing the alloying is still under active investigation. Some of these are shown in Figure 6.[4] European foundries are trying closed ladles under pressure to improve efficiency. In most foundries the inoculation smoke is vented through the roof as with other emissions in the melt shop.

The control of emissions has been recommended by the American Foundrymen's Society (AFS).[20] However, no references have been found, in this or other studies, indicating the extent of emission control systems for inoculation in actual use. The AFS book on environmental control shows local exhaust hoods fitted to cupolas that pour the iron directly into small ladles, presumably using the pour over technique of adding iron to an empty ladle containing the inoculant. This would be such an inefficient method of inoculation that economics would prohibit its use in large scale production. Other sources have suggested control devices that would be applicable only to small scale, infrequent inoculation practice.

A. T. Kearney[4] has reported one case of measured inoculation emissions, which are presented in Table 3. The analysis was reported to them by a foundry they visited.

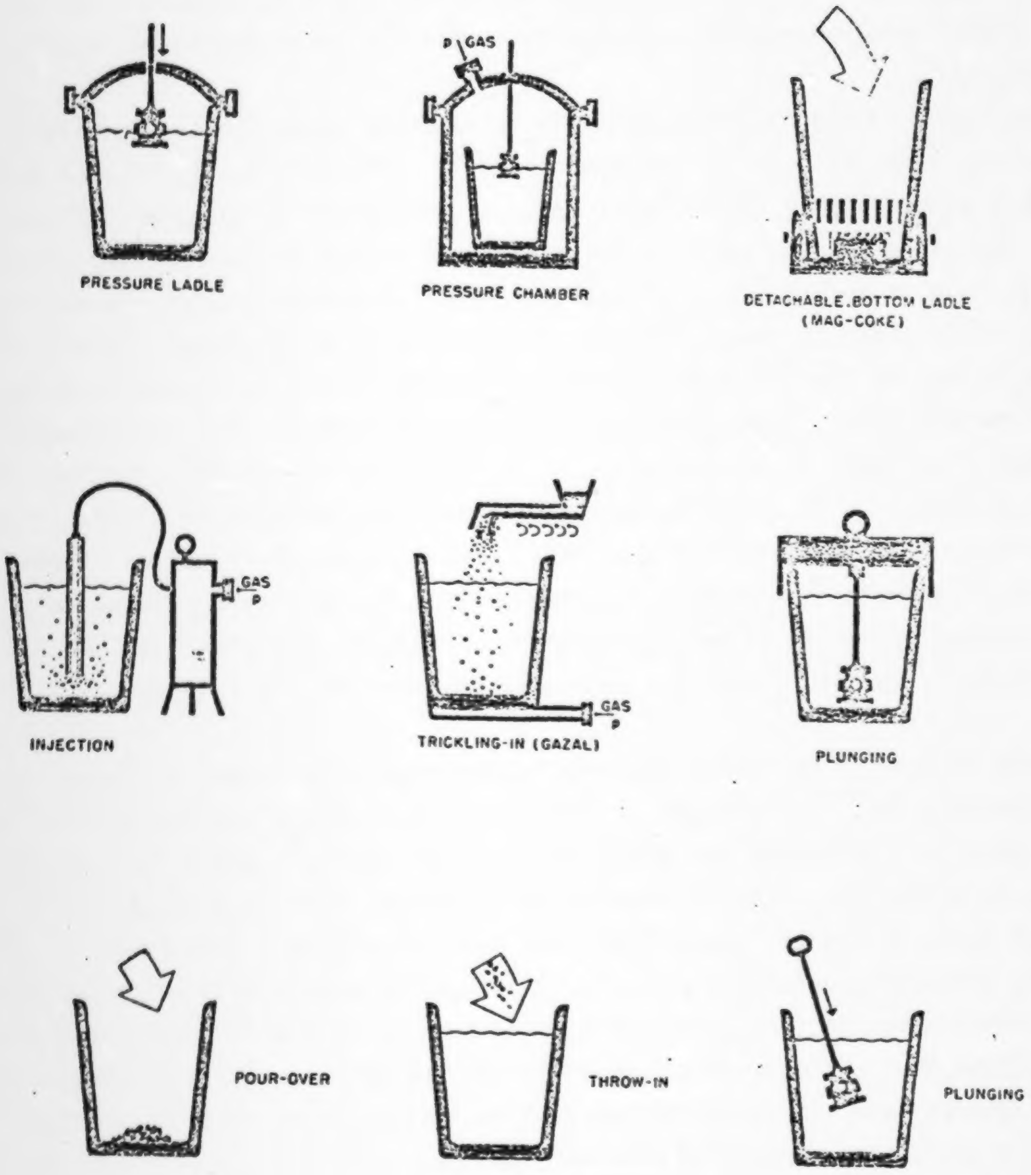

PRESSURE LADLE
P GAS
PRESSURE CHAMBER
DETACHABLE BOTTOM LADLE (MAG-COKE)
GAS P
INJECTION
GAS P
TRICKLING-IN (GAZAL)
PLUNGING
POUR-OVER
THROW-IN
PLUNGING

Figure 6. Illustration of magnesium treatment methods for producing ductile iron.[4]

TABLE 3. MAGNESIUM TREATMENT SYSTEMS EMISSIONS REPORT FOR DUCTILE IRON PRODUCTION AND GRAY IRON DESULFURIZATION[4]

Iron Treated 30 tons per hour

Inoculant Added - 20-22 pounds per ton Iron

Inoculants Used - MgFeSi - (10% Mg)
75% FeSi
Soda Ash

Emissions Produced - 100 pounds per hour
3.3 pounds per ton iron

Emissions Analysis - 32% MgO
18.7% Fe_2O_3
9.5% CO_2
4.2% SiO_2
2.5% S
1.1% C
0.6% CaO
Balance Na_2O

In large operations of ductile iron production the metal is desulfurized before inoculation. This is frequently done by calcium carbide additions. Failure to desulfurize results in desulfurization by the magnesium, which can be a very expensive method.

Mold inoculation is practiced to a lesser degree, when possible. In some cases, a powder of magnesium or its alloys is spooned into the mold cavity in the drag mold. More elaborate methods involve using "plugs" of inoculant, made of iron, magnesium, ferrosilicon and additive elements, which are anchored into the mold. The mold is specially designed for this type of casting. Since the inoculation occurs during the casting process, fading is not a problem so less material can be used.

At the present time, inoculation seems to involve as much art as science, for procedures that work at one foundry do not work at another because of variables in operating time, temperature, casting size, and metal chemistry. The industry's prime concern is the metallurgical result. Environmental pollution from inoculation is being indirectly attacked by seeking more efficient methods that would result in reduced need for control. Some have suggested that control can be effected with hoods and fabric filters. In the case of very small operations this may be true, but the larger operations are not physically amenable to conventional control techniques and may require new engineering designs for the inoculation facilities with the intent of making them amenable to control.

The Nature of Inoculation Smoke

The burning magnesium from inoculation is commonly referred to as MgO.[4] According to the chemical literature,[3] burning magnesium in air will also produce:

a. MgO_2 magnesium peroxide,
b. Mg_3N_2 magnesium nitride.

The fact that magnesium burns in nitrogen, as well as several fire extinguishing gases and liquids, is known, and one can expect to find a considerable amount of Mg_3N_2 in the inoculation smoke. This could have adverse environmental or health effects because on contact with water the magnesium nitride produces ammonium hydroxide and magnesium hydroxide:

$$Mg_3N_2 + 8H_2O \rightarrow 3\,MgO \cdot H_2O + 2NH_4OH.$$

If this reaction occurs in the lungs or breathing passages, the Mg_3N_2 dust would deposit NH_4OH ($pH > 11.6$) and $Mg(OH)_2$ (pH 10.5) which are caustic to the mucous membranes.

The magnesium oxide, MgO, formed can exist in two forms.[13] MgO formed at "low temperature" will hydrolyze readily by the reaction $MgO + H_2O \rightarrow MgO \cdot H_2O$ (or $Mg\,(OH)_2$), and the hydroxide dissolves slightly forming a solution of pH 10.5. This is known to be corrosive to paint. While the alkalinity may be undesirable, it is conceivable that small quantities of MgO in the lungs could be eliminated from the body because of its solubility.

When MgO is formed at "high temperatures," (commercially known as "dead burnt") it does not hydrolyze or react within reasonable times, such as one year. This suggests that it would be classified as insoluble inhalable particulate. Which form of MgO is emitted from the inoculation process is not known.

Magnesium also reacts with oxygen to form the peroxide, MgO_2. There is no data on the quantity of this substance that can be expected to form from inoculation.

Another topic of environmental concern that has not been addressed is the fate of inoculation additives. The effects of fading are reduced by adding Ba, Ce, Ca, Nd, Pr. In addition, metallurgical problems with heavy sections that require up to 3 hours to cool are alleviated by adding Sr and Zr.[88] These metals have been detected in the shakeout smoke, as will be noted in the sampling analysis section of this report. It is reasonable to assume that much larger quantities are present in the smoke from inoculation itself.

5.2.5 Pouring

In nearly all cases, iron castings are made by pouring the liquid metal into the molds under human guidance. Totally automatic systems have been designed but are seldom used, even in the large automotive foundries. Each different job, or type of casting, will require pouring different amounts of metal into a hole that has different positions. If the gate is blocked, or other faults occur within the mold during the pouring operation. an operator can detect such problems visually and stop the metal flow. Such ability has not yet been programmed into a machine.

In the simplest case, iron is tapped from the cupola or electric furnace into a small ladle of 1/3 to 1 ton capacity. The ladle usually hangs from an overhead conveyor controlled by a switch box on or near the ladle carrier. The pouring man moves the ladle along the conveyor line of moving molds, and when he has positioned the ladle with respect to the mold, turns a large steering wheel tilting the ladle and pouring the metal into the sprue hole. In foundries that do extensive ductile iron casting, the metal is tapped from the furnace to a desulfurizing ladle, then to an inoculation ladle. After inoculation the large ladle is transported to a point adjacent to the pouring station and is used to refill the pouring ladles, several of which may be in operation at a given time. In foundries that do limited ductile iron casting, inoculants may be added to the pouring ladle just prior to tapping the furnace.

Emissions from pouring can be successfully captured by two methods. The most convenient method for a large foundry is the hooded pouring station, shown in Figure 7.[90] In this type of hood, air is blown down from the front edge and sucked up by the lower grill. A push pull system utilizing an

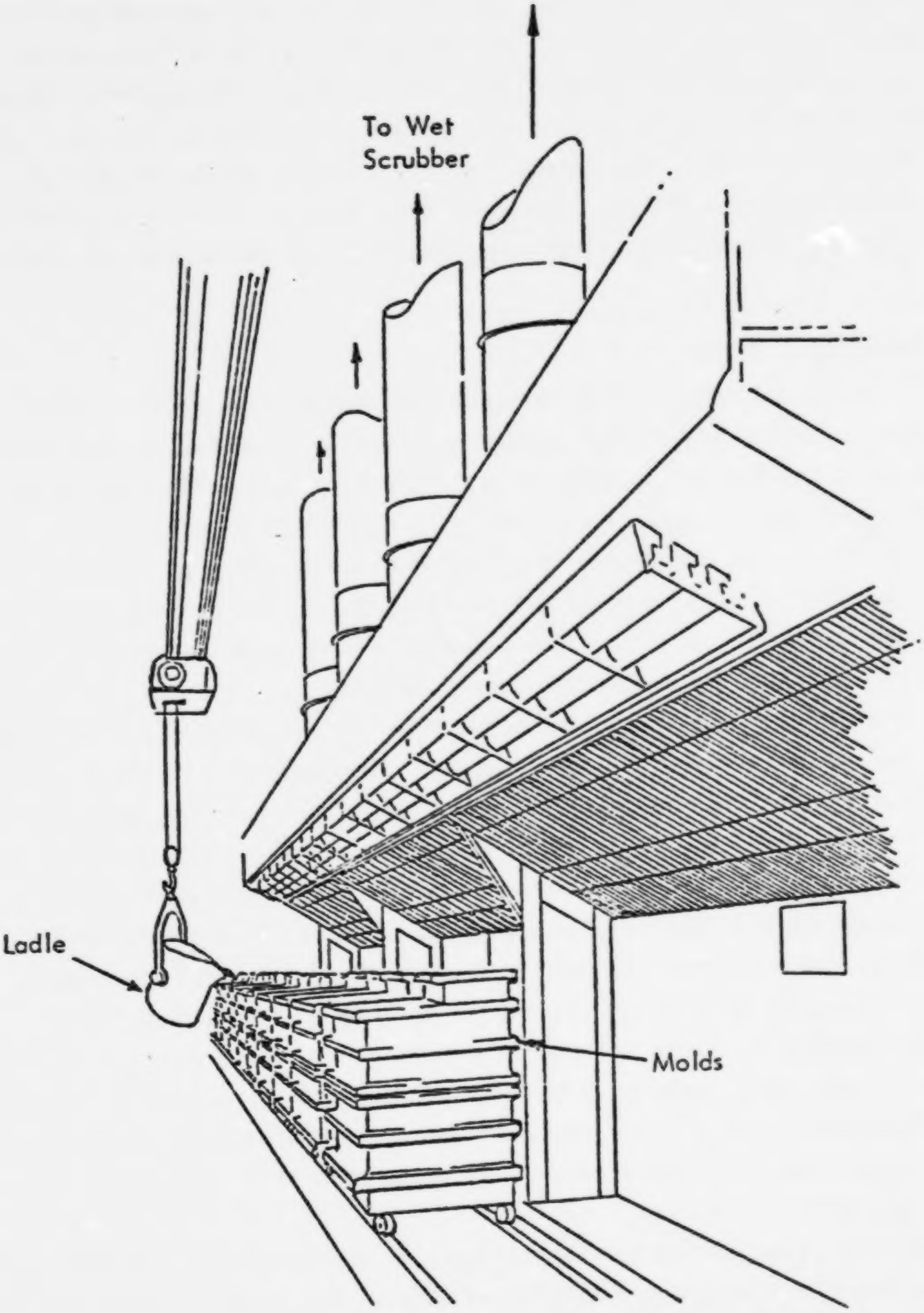

To Wet Scrubber
Ladle
Molds

Figure 7. Hooded pouring station.[90]

incoming draft from a floor grating which is drawn out by the hood is also very effective. Smaller foundries can use a portable exhaust hood as shown in Figure 8.[20]

Pouring and cooling are areas of concern from an emissions standpoint. During the pouring operation, the mold and core are usually enclosed in a flask. Within seconds of pouring, emissions are evolved. A controlled laboratory test with an uncored, green-sand mold containing 5 percent seacoal, in which a 30 pound 4 in. cube was cast was performed by Bates and Scott.[21] The carbon monoxide concentrations peaked at about 1900 ppm after 5 minutes and the total hydrocarbons maximized at 1225 ppm after 6 minutes. The sand to metal ratio was 3:1.

The same study used green sand molds with various formulations of core sand. Maximum values were reached after 1 to 5 minutes for carbon monoxide, 1 minute for carbon dioxide, 1 to 5 minutes for methane, and 1 to 6 minutes for total hydrocarbons. Particulate emissions were 0.0625 grains/scf (142 mg/m^3) during solidification. Peak particle counts ($3x10^4$) of 0.35 to 1.0 mm sized particles occured approximately 11 minutes after pouring.[21]

The experiments of Bates and Scott that most closely approximate the pouring conditions were the sealed flask experiments. The effluent they collected from flasks after pouring, was analyzed by GC-MS and several carcinogenic compounds were identified. Unfortunately no quantification was performed.

Section 9 of this report discusses the findings of RTI's sampling in terms of the mechanisms involved in the emission of organic vapors from the casting processes. According to the operative mechanism discussed, the maximum emission of higher molecular weight (HMW) substances should occur during pouring and initial cooling, with the release of HMW substances in shakeout being a function of metal temperature. There are moderating factors: in the first instance, the major organic vapor emission on pouring will be from the top surface of the sand around the sprue hole. The majority of the gases formed at the sand metal interface will have to pass through the sand to escape, with the HMW compounds being trapped, as explained in Section 9. Secondly, large quantities of H_2, CO, and CH_4 are produced and at the time of pouring these ignite. The burning gases may be seen for several minutes after pouring. Since the HMW compounds that escape will be entrained in

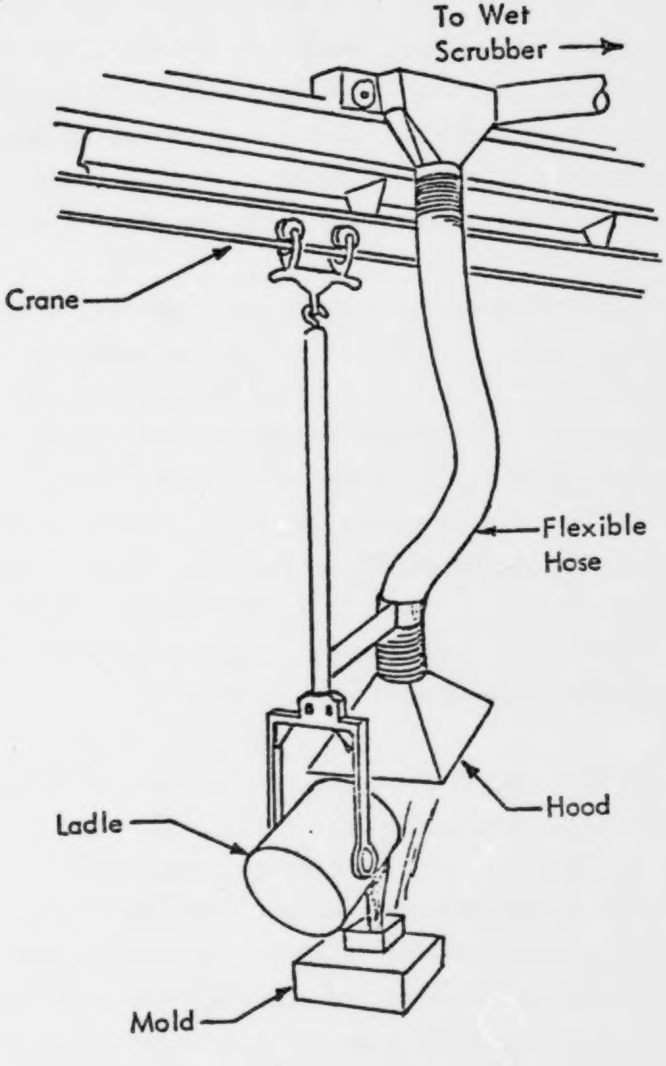

To Wet Scrubber
Crane
Flexible Hose
Hood
Ladle
Mold

Figure 8. Moveable pouring hood.

this release of gases, they will be burned along with the lighter gases, thereby destroying some of them. Thus the unignited emissions from pouring are the most probable source of HMW organic emissions.

5.2.6 Cooling

After pouring, on an automated casting line, the molds are conveyed to a cooling room. In this room the conveyor system is designed to provide maximum track length, or in terms of operating conditions, time delay. Cooling time varies from 45 minutes to 2 hours on the automated lines and may extend to overnight in small nonautomated foundries. In some places the cooling occurs in a tunnel rather than a room. No literature data have been found on cooling times but obviously it will vary with the size of the casting and the degree to which production is "pushed." Foundries have been observed operating at twice their design capacity, which means the cooling time has been reduced from the original design value.

This study has learned, as indicated in Section 9, that cooling time is a major factor in shakeout emissions. One foundry visited was casting at less than design capacity and cooling for 2 hours. The shakeout emissions were wet scrubbed and blown into the cooling room, from which they were vented through the roof. No noticeable odor was present in the cooling room. It should be noted that the foundry had an unusually large ventilating system that changed the air in the building 20 times per hour. The ventilating system, however, was a major noise source.

5.2.7 Shakeout

The most elementary method of removing castings from a mold is to dump the mold, and hook, or pull out, the casting from the sand. When significant production is required, the molds are automatically inverted and dumped onto a vibrating grating which shakes out the sand and separates the casting. The sand falls through the grating and onto a conveyor belt which carries it to the conditioning and reprocessing system. In some cases the shakeout can be a long vibrating grate (30 meters), such as for gasoline engine blocks and heads, where much internal core sand must be removed. There are many variations of shakeout systems, including heavy screen drums that rotate batches of castings and long cylindrical perforated cylinders that tumble the parts and process parts continuously.

The shakeout has the potential to generate the most fumes of the many foundry operations. By the time the mold assembly reaches the shakeout, the bulk of the thermal decomposition of the mold/core materials has occurred. The products of thermal decompositon will tend to be lower molecular weight materials and will vaporize and diffuse away from the hot metal-sand interface into the cooler sand. The physical chemistry of the situation predicts that some of the organic emissions will condense and adsorb on the cooler sand of the mold. Most compounds boiling below 100°C will be lost in cooling. During shakeout, the cooler sand comes into contact with the hot sand surrounding the metal, and the metal itself. This causes a flash boiling, thereby producing an emission of the pyrolysis products. In addition, there will be a lesser amount of decomposition (than occurs during pouring) of the organic constituents. This is discussed fully in Section 9. The experiments of Bates and Scott showed higher peak hydrocarbon emissions (1500 ppm) during shakeout than during pouring and cooling, although the average concentrations were lower during shakeout. The particulate emissions during these laboratory tests were 55 percent higher with a 10 fold particle count increase over those of pouring. Toeniskoetter and Schafer sampled many foundries for selected emissions from different binder systems.[93] Their results show that the isocyanate concentration is frequently greater at shakeout than at the pouring station.

5.2.8 Finishing

After castings are removed from the molds the sprues, gates, and risers must be broken off. If the separate parts of the mold did not mate perfectly, there may be a "flash" or sharp edge. The final finishing is done by grinding off these imperfections. The surface of the casting may also be cleaned by shot blasting.

The emissions from these processes are relatively coarse and easily controlled by dry mechanical collectors and baghouses.[4]

6.0 WASTE STREAM CHARACTERISTICS

Foundries have long been recognized for their visible air emissions, and sometimes for their obnoxious odors. In terms of quantity, solid waste in the form of sand is the major pollutant emitted, but there are many other emissions. (Table 4). After solid waste, particulate emissions are the most prevalent with water pollution generally a secondary problem to particulates control. Water that is used to scrub the air picks up contaminants, most of which can be removed by settling tanks and the remaining soluble organics are removed by digestion in holding ponds.

6.1 SOLID WASTES

The solid wastes that are produced by a foundry consist of used core and molding sand, slag and refractories from iron melting, and dust and other particulates collected by the air scrubbers (Figure 9).

Over 75 percent of the foundry generated solid waste is from the core making and molding operations with the remainder coming from melting operations and emissions control processes.[23-27] This waste can be divided into the following categories:

- Refractories
- System sand (including molding and core sand dilution)
- Core sand (butts and sweepings not entering the system sand)
- Annealing room waste (in malleable iron foundries)
- Cleaning room waste
- Slag
- Coke ash (collected particulates)
- Scrubber discharge
- Dust collector discharge
- Miscellaneous

Details of the material balances of these wastes have been determined.[23-25]

Tables 5 through 11 present data on the magnitude of materials movement from three foundries.[22] Foundry 1 is a malleable iron operation using

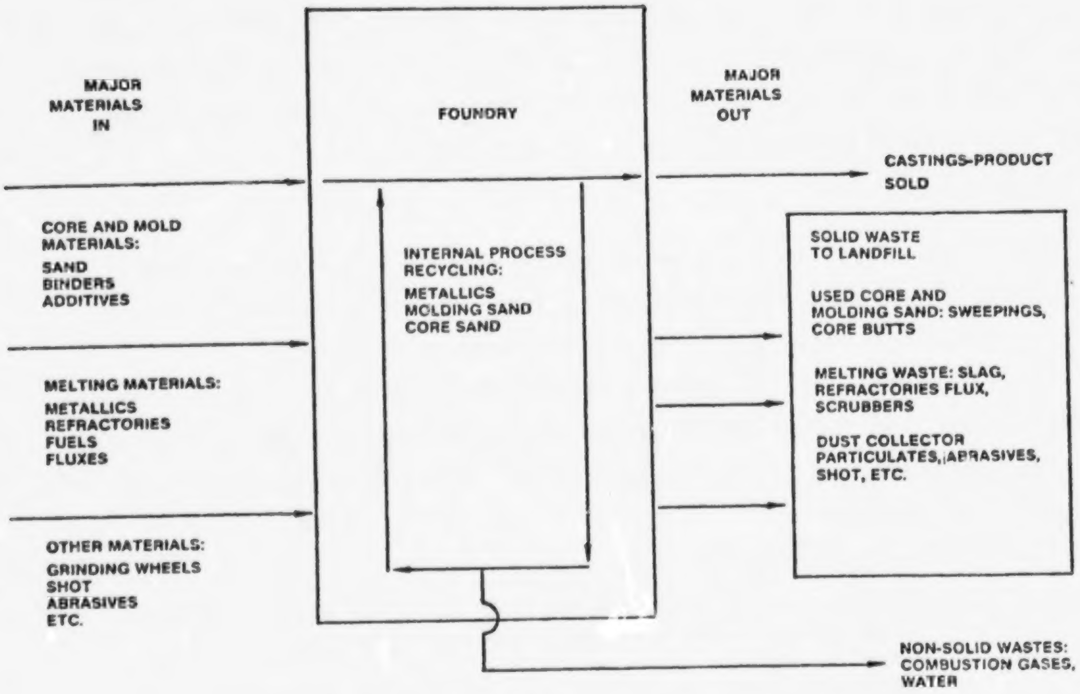

MAJOR MATERIALS IN
FOUNDRY
MAJOR MATERIALS OUT
CASTINGS-PRODUCT SOLD
CORE AND MOLD MATERIALS:
SAND
BINDERS
ADDITIVES
INTERNAL PROCESS RECYCLING:
METALLICS
MOLDING SAND
CORE SAND
SOLID WASTE TO LANDFILL
USED CORE AND MOLDING SAND: SWEEPINGS, CORE BUTTS
MELTING WASTE: SLAG, REFRACTORIES FLUX, SCRUBBERS
DUST COLLECTOR PARTICULATES, ABRASIVES, SHOT, ETC.
MELTING MATERIALS:
METALLICS
REFRACTORIES
FUELS
FLUXES
OTHER MATERIALS:
GRINDING WHEELS
SHOT
ABRASIVES
ETC.
NON-SOLID WASTES: COMBUSTION GASES, WATER

Figure 9. Balance of major solid materials entering and leaving the sand foundry.[22]

TABLE 4. CHARACTERISTICS AND SOURCES OF EMISSIONS IN VARIOUS FOUNDRY DEPARTMENTS[21]

Department	Operation	Type	Emissions+ Concentration	Particle+ Size (Microns)	Relative+ Controllability	Relative+ Cost
Molding, Pouring, and Shakeout	Molding	Sand Dust Vapor	Light	Coarse	Easy	Low
	Pouring	Core oil vapors	Heavy		Moderate	Medium
	Cray and ductile iron	Facing Fumes	Heavy			
	Malleable	Metal oxides	Light	Fine to medium		
		Flouride fumes	Heavy	0.01 to 0.4		
		Magnesium oxide fumes	Heavy			
		Synthetic binder smoke and fumes	Moderate to heavy			
	Shakeout	Sand fines	3 to 5 gr/cu ft	50%-2 to 15	Moderate	Medium
		Smoke	Heavy	0.01 to 0.4		
		Steam	Heavy			
		Dust	3 to 5 gr/cu ft	50%-2 to 15		
Cleaning and Finishing	Abrasive cleaning	Dust	3 gr/cu ft and up	50%-2 to 15	Easy	Low
	Grinding	Metal dust	5 gr/cu ft and up	Above 7	Medium	Low
		Sand fines	3 to 5 gr/cu ft	Fine to medium		
		Abrasives	0.5 to 2 gr/cu ft	50%-2 to 7		
		Wheel Bond material	Light	Fine		
		Vitrified resins	Light	50%-2 to 15		

(continued)

TABLE 4. (cont'd)

Department	Operation	Type	Emissions[+] Concentration	Particle[+] Size (Microns)	Relative[+] Controllability	Relative[+] Cost
	Annealing and heat treating	Oil vapors		0.03 to 1	Moderate	Low
	Painting spray and dip	Volatile fumes			Easy	Low
		Paint spray carryover	0.5 to 2 gr/cu ft	50%-2 to 7		
		Water spray carryover				
Sand Conditioning	New sand storage	Fines	3 to 5 gr/cu ft	50%-2 to 15	Moderate	High
	Sand handling system	Fines	3 to 5 gr/cu ft	50%-2 to 15	Moderate	Medium
		Steam				
	Screening	Fines	3 to 5 gr/cu ft	50%-2 to 15	Easy	Low
	Mixing	Fines	3 to 5 gr/cu ft	50%-2 to 15	Easy	Medium
		Flour	Moderate	Fine to medium		
		Bentonites	Moderate	Fine to medium		
		Sea Coal	Moderate	Fine to medium		
		Cellulose	Moderate	Fine to medium		
	Drying and reclamation	Dust	1/2 to 2 gr/cu ft	50%-7 to 15	Easy	Medium
		Oil vapors		0.03 to 1		
Coremaking	Sand storage	Sand fines	Heavy	Fine	Moderate	High
		Flour	3 to 5 gr/cu ft	50%-7 to 15		
		Binders				
	Coremaking	Sand fines	Heavy	Fine to medium	Moderate	Medium
		Dust	Light	Fine to medium		
	Baking	Vapors Smoke			Easy	Medium

[+] Represents the view of Bates and Scott, reference 21.

TABLE 5. POUNDS OF NEW MATERIAL PURCHASED PER YEAR BY CATEGORY[22]

Foundry	Malleable 1	Ductile Iron 2	Gray and Ductile Iron 3
A. Refractories	200,200	728,100	530,000
B. Sand used directly in molding system			
1. New Sand	3,492,000	20,546,000	4,725,800
2. Clay	1,012,800	3,677,700	2,160,000
3. Carbon	387,300	734,300	1,584,000
Subtotal	4,892,000	24,938,000	8,469,800
C. Sand used as Cores			
1. Shell Sand	558,000	3,976,000	1,800,700
2. Oil Sand	2,243,800	4,076,000	15,200,600
3. No-Bake			3,540,000
4. CO_2 Sand			2,688,000
Subtotal	2,801,800	8,052,000	23,236,300
Total Sand Binder and Additives	7,693,000	32,990,000	31,707,100
D. Metal	27,805,000	63,209,000	122,205,000
E. Miscellaneous	25,800		
F. Annealing Room	220,000		
G. Cleaning Room			
1. Grinding	13,800	129,000	29,300
2. Steel Shot	49,100	126,000	216,000
3. Other	5,400		6,000
Subtotal	68,300	255,000	251,300
H. Slag Floculant	38,900	1,396,000	
I. Flux		5,658,000	8,544,000
J. Scrubber Line		32,500	400,000
K. Coke		8,672,000	27,516,000
Other	101,800	1,200	
TOTAL	36,153,800	112,941,800	185,153,900

TABLE 6. PERCENTAGE OF MATERIAL PURCHASED BY CATEGORY EXCLUDING METAL MELTED[22]

Foundry	Malleable 1	Ductile Iron 2	Gray and Ductile Iron 3
A. Refractories	2.40	1.46	0.84
B. Sand used directly in molding system			
1. New Sand	41.83	41.31	7.51
2. Clay	12.13	7.39	3.43
3. Carbon	4.64	1.48	2.52
Subtotal	58.60	50.14	13.46
C. Sand used as Cores			
1. Shell Sand	6.68	7.99	
2. Oil Sand	26.87	8.20	24.16
3. No-Bake			5.62
4. CO_2 Sand			4.27
Subtotal	33.55	16.19	34.05
Total Sand Binder and Additives	92.15	66.33	50.37
E. Miscellaneous	1.53		
F. Annealing Room	2.64		
G. Cleaning Room			
1. Grinding	0.17	0.26	0.05
2. Steel Shot	0.59	0.25	0.34
3. Other	0.06		0.01
Subtotal	0.82	0.51	0.40
H. Slag Floculant	0.46	2.81	
I. Flux		11.38	13.57
J. Scrubber Line		0.07	0.64
K. Coke		17.44	34.18
TOTAL	100.00	100.00	100.00

TABLE 7. POUNDS OF NEW MATERIAL CONSUMED ANNUALLY PER TON OF METAL MELTED (BASED ON NEW PURCHASES)

Foundry	Malleable 1	Ductile Iron 2	Gray and Ductile Iron 3
A. Refractories	14.40	23.04	8.67
B. Sand used directly in molding system			
1. New Sand	251.18	649.51	77.34
2. Clay	72.85	116.39	35.35
3. Carbon	27.85	23.20	25.93
Subtotal	351.88	789.10	138.62
C. Sand used as Cores			
1. Shell Sand	40.14	125.80	29.47
2. Oil Sand	161.40	128.96	248.90
3. No-Bake			57.94
4. CO_2 Sand			43.99
Subtotal	201.54	254.76	380.30
Total Sand Binder and Additives	553.42	1043.86	518.92
D. Metal	2000.00	2000.00	2000.00
E. Miscellaneous	9.17	0.04	
F. Annealing Room	15.82		
G. Cleaning Room			
1. Grinding	0.99	4.08	0.48
2. Steel Shot	3.53	3.99	3.54
3. Other	0.39		0.10
Subtotal	4.91	8.07	4.12
H. Slag Floculant	2.80	44.17	
I. Flux		179.03	139.83
J. Scrubber Line		1.03	6.55
K. Coke		274.39	352.13
TOTAL	600.52	1573.63	1030.22

TABLE 8. ESTIMATED POUNDS OF MATERIAL TO LANDFILL PER YEAR BY CATEGORY[22]

Foundry		Malleable 1	Ductile Iron 2	Gray and Ductile Iron 3
A.	Refractories	200,200	728,100	530,000
B.	System Sand			
	1. Molding Sand from New Material	1,924,100	23,600,000	20,351,600
	2. Degraded Shell	195,300	6,623,200	382,000
	3. Degraded CO_2	617,600		570,300
	4. Degraded Oil	503,000		3,226,700
	5. Degraded No-Bake			751,000
	Subtotal	6.240,000	30,222,200	25,281,600
C.	Core Sand Total			
	1. Core Butts	1,315,900	1,168,800	4,929,900
	1. Core Room Sweepings	250,000	260,000	1,790,400
	Subtotal	1,565,900	1,428,800	6,720,300
	Total Sand	7,805,900	31,652,000	32,001,900
D.	Annealing Room Waste	220,000		
E.	Cleaning Room Waste			
	1. Grinding	13,800		29,300
	2. Steel Shot	49,100		216,000
	3. Other	5,400		6,000
	Subtotal	68,300	1,205,900	251,300
F.	Slag	480,000	5,460,000	7,968,000
G.	Coke Ash		882,800	2,190,000
H.	Scrubber Discharge			1,032,000
I.	Dust Collector	100,000		4,800,000
J.	Miscellaneous	25,200		
TOTAL		8,899,600	39,928,800	48,773,200

TABLE 9. ESTIMATED PERCENTAGE OF MATERIAL TO LANDFILL PER YEAR BY CATEGORY*[22]

Foundry	Malleable 1	Ductile Iron 2	Gray and Ductile Iron 3
A. Refractories	2.25	1.82	1.09
B. System Sand			
1. Molding Sand Materials	55.34	59.11	41.72
2. Degraded Shell	2.19	16.59	0.78
3. Degraded Oil	5.65		6.62
4. Degraded CO_2	6.94		1.17
5. Degraded No-Bake			1.54
Subtotal	70.12	75.70	51.83
C. Core Sand Total			
1. Core Butts	14.79	0.65	10.11
1. Core Room Sweepings	2.81	2.93	3.67
Subtotal	17.60	3.58	13.78
Total Sand	87.72	79.28	65.61
D. Annealing Room Waste	2.47		
E. Cleaning Room Waste			
1. Grinding	0.16		0.06
2. Steel Shot	0.55		0.44
3. Other	0.06		0.01
Subtotal	0.77	3.02	0.51
F. Slag	5.39	13.67	16.34
G. Coke Ash		2.21	4.49
H. Scrubber Discharge			2.12
I. Dust Collector Discharge	1.12		9.84
J. Miscellaneous	0.28		
TOTAL	100.00	100.00	100.00
Total Sand Percentage Excluding Slag, Coke Ash and Refractories	95.0	96.3	83.0

*This table is expressed as a percentage of Table 8 adjusting to exclude losses resulting from processes such as coke conversion, etc.

TABLE 10. ESTIMATED POUNDS OF MATERIAL TO LANDFILL PER TON OF METAL MELTED[22]

Foundry	Malleable 1	Ductile Iron 2	Gray and Ductile Iron 3
A. Refractories	14.40	23.05	8.67
B. System Sand			
1. Molding Sand - New Material	354.19	537.16	333.08
2. Degraded Shell	14.05	209.57	6.25
3. Degraded Oil	36.18		52.81
4. Degraded CO_2	44.42		9.33
5. Degraded No-Bake			12.29
Subtotal	112.63	45.21	109.98
C. Core Sand Total			
1. Core Butts	94.65	36.98	80.68
1. Core Room Sweepings	17.98	8.23	29.30
Subtotal	112.63	45.21	109.98
Total Sand	561.47	791.94	523.74
D. Annealing Room Waste	15.82		
E. Cleaning Room Waste			
1. Grinding	0.99		0.48
2. Steel Shot	3.53		3.54
3. Other	0.39		0.10
Subtotal	4.91	38.16	4.12
F. Slag	34.53	172.76	130.50
G. Coke Ash		27.93	35.85
H. Scrubber Discharge			16.89
I. Dust Collector Discharge	7.19		78.56
J. Miscellaneous	1.81		
TOTAL	640.13	1053.84	798.33

TABLE 11. ESTIMATED POUNDS OF MATERIAL TO LANDFILL PER TON OF METAL SHIPPED[22]

Foundry	Malleable 1	Ductible Iron 2	Gray Iron Ductible Iron 3
A. Refractories	40.25	52.80	17.96
B. System Sand			
1. Molding Sand - New Material	989.76	1711.32	689.68
2. Degraded Shell	39.26		12.94
3. Degraded Oil	101.11	480.27	109.34
4. Degraded CO_2	124.14		19.33
5. Degraded No-Bake			
Subtotal	1254.27	2191.59	856.74
C. Core Sand Total			
1. Core Butts	264.50	84.75	167.06
1. Core Room Sweepings	50.25	18.85	60.67
Subtotal	314.75	103.60	227.73
Total Sand	1569.08	2295.19	1084.45
D. Annealing Room Waste	44.22		
E. Cleaning Room Waste			
1. Grinding	2.77		0.99
2. Steel Shot	9.87		7.32
3. Other	1.09		0.20
Subtotal	13.73	87.44	8.51
F. Slag	96.48	395.92	270.02
G. Coke Ash		64.02	74.22
H. Scrubber Discharge			34.97
I. Dust Collector Dicharge	20.10		162.67
J. Miscellaneous	5.06		
TOTAL	1788.86	2895.36	1652.83

induction melting; Foundry 2 produces gray and ductile iron using basic practice cupola melting; and Foundry 3 also produces gray and ductile iron using a cupola for primary melting and duplexing into induction furnaces.

6.2 PARTICULATE EMISSIONS

The effect of cupola emissions on the surrounding environment caused serious examination of particulate emissions by the Public Health Service in 1968 and the A. T. Kearney Co. in 1971.[4] At that time the major furnaces in operation were cupolas and EAFs. It was determined that 10.4 kg/metric ton (20.8 lb/ton) of particulate emissions were produced by the cupolas and 6.9 kg/metric ton (13.8 lb/ton) from the EAFs. There are no reasons for these emission factors to be different today, but the emissions to the environment have been reduced by the addition of air pollution control devices on the cupolas and EAFs and also some foundries have changed to the induction furnace. When charged with clean metal, the induction furnace produces virtually no emissions.

Particulate emissions have been measured in a laboratory apparatus by Bates and Scott,[21] whose data are presented in Table 12. Interpretation of their data requires care. In the first instance, as revealed by the columns of cumulative summation (summed by RTI), for particles greater than 0.54 μm, the total mass of particulate from pouring exceeds that from the shakeout. Bates and Scott also determined the dust loadings, over the 30 minute cooling interval after pouring and the 25 minute interval after shakeout. This exhibited an average of 142 mg/m^3 of pouring and cooling emissions and 221 mg/m^3 of shakeout emissions, 56% higher than the pouring emissions. An optical particle counter was used to determine the time profile of dust concentration from 0.35 to 1.00 micron particles. This showed a peak concentration of 3×10^4 particles per cubic centimeter after pouring and 3×10^5 $particles/cm^3$ after shakeout. These laboratory results coincide in principle with A. T. Kearney's estimates of shakeout emissions (32 lb/ton melt or 16 kg/tonne) being greater than pouring emissions (5.1 lb/ton melt or 2.55 kg/tonne).

As a result of the visible nature of particulate emissions and the imposition of environmental control regulations, most foundries have installed particulate control systems. These systems do not control organic

TABLE 12. PARTICLE SIZE DISTRIBUTIONS OF GREEN SAND EMISSIONS FOR 4" CUBE PATTERN[21]

	Pouring			Shakeout		
Size (microns)	Mass (g)	Σ	% of Total	Mass (g)	Σ	% of Total
Less than 0.54	3.98	3.98	7.0	5.14	5.14	24.0
0.54-0.83	8.35	12.33	14.8	2.28	7.42	10.6
0.84-1.34	23.01	35.34	40.7	1.36	8.78	6.3
1.35-2.67	16.69	52.03	29.5	0.36	9.14	1.7
2.68-4.14	1.86	53.89	3.3	0.56	9.7	2.6
4.15-6.08	.97	54.86	1.7	0.24	9.94	1.1
6.09-8.95	.53	55.39	0.9	10.88	20.82	50.7
8.96-14.36	.40	55.79	0.7	0.34	21.16	1.6
More than 14.36	.68	56.47	1.2	0.28	21.44	1.3

TABLE 13. RANGES OF POLLUTANTS IN SELECTED WASTES[22]

Component	Foundry Leachate	Urban Landfill Leachate	Septic Tank Effluent
Organic carbon (mg/l)	4-185	250-28,000	25-200
COD (mg/l)	25-1,100	100-51,000	250-1,000
Phenol (μg/l)	12-400	---	0-300*
Cyanide (μg/l)	20-80	---	---
Sulfate (mg/l)	30-1,200	25-1,500	10-600
Fluoride (mg/l)	3-120	---	0-10
Iron (mg/l)	0.1-0.5	200-1,700	0-20
Zn (mg/l)	0.1-15	1-135	0.15*
Ni (mg/l)	0-0.6	0.01-0.8	0.02
Cu (mg/l)	0.02-1.6	0.1-10	0.1*
pH	7.2-10.0	4-9	6.8-8.5

*Municipal Wastewater Effluents

vapor emissions however, and that is a problem of concern. Some foundries, especially high capacity companies operating in densely populated areas, have installed chemical scrubbers. These not only reduce pollution but also allow the air to be recycled within the plant, which in some cases saves energy. Chemical scrubbers are not in significant use and add to the economic burden on a company.

Further discussion of organic emissions to the air is presented in Section 6.4.

6.3 WATER EFFLUENTS

The only effluents from foundries are indirect, i.e., resulting from the air pollution control systems. Larger foundries remove the sand and dust from the scrubber discharge in a clarifier tank and landfill it. The remaining water goes to a settling pond and often flows from the pond to a river. Sometimes some of the pond water is recirculated to the scrubbers. Although no specific data was found, it is known that there is a problem with phenols in foundries using phenol-based chemical binders, unless their ponds provide adequate holding time for biological action.

The major source of industry water pollution is in the form of leachate from discarded sand. An extensive study undertaken by the American Foundrymen's Society showed that the major emission occurs within a 1-2 year period. Table 13 is a comparison of the pollutant ranges for selected wastes and Table 14 is a summary of the AFS laboratory analyses.[22]

6.4 POTENTIAL POURING AND SHAKEOUT DISCHARGES

The major concern of the sampling effort undertaken during this study was the determination of the nature and quantity of discharges resulting from the pyrolysis of the organic materials used in sand casting. The results of a literature study presented in this section and Appendix A and indicate that environmentally undesirable organic compounds could be released as a consequence of using organic binders and additives in the molds.

When molten iron is poured into a sand mold, the temperature reached by the sand varies according to the distance from the sand-metal interface. Figure 10 presents time-temperature curves for the metal and sand at various distances from the metal determined in a laboratory study of clays.[28]

TABLE 14. LYSIMETER RESULTS--18 SIMULATED MONTHS[22]

	Concentrations in Leachate/Foundries								
	Foundry 1			Foundry 2			Foundry 3		
Component	max	1 yr	18 mo	max	1 yr	18 mo	max	1 yr	18 mo
Organic carbon (mg/l)	14	5	4	31	15	13	185	35	27
COD (mg/l)	75	30	25	240	100	90	1100	260	260
Phenol (μg/l)	25	14	12	78	16	15	52	18	15
Cyanide (μg/l)	--	--	--	80	---	<20	<20	---	<20
Fluoride (mg/l)	3	--	--	32	25	20	3	---	---
Sulfates (mg/l)	30	--	--	1220	---	(800)	78	---	---
pH Range	7.6-8.0→			8.0-8.8→			7.3-8.0↓		

( )-Estimate value

↑↓ -Increase/decrease

→ - Steady

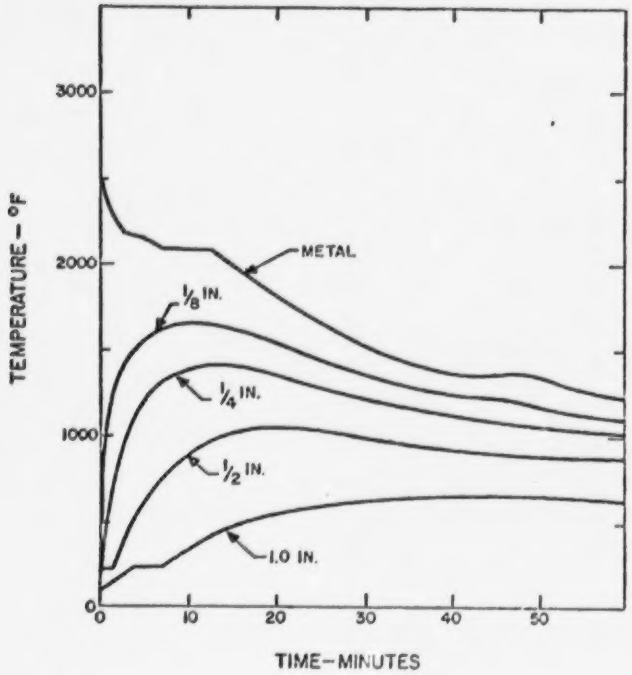


Figure 10. Temperature Levels in Sand at Various Distances from the Metal/ Sand Interface[1] (Reprinted from AFS Transactions, 1976)[28]

It can generally be assumed that organic compounds will begin to decompose above 400° C. Thus, binders and additives will undergo some degree of thermal decomposition at the sand-metal interface and for a distance of 1.9 to 2.5 cm (3/4 to 1 in) away from the interface. Some of the decomposition products may be gaseous at room temperature, 25° C (77° F) and will pass through the sand escaping into the atmosphere. Other pyrolysis products will pass into the cooler sections of the sand and condense to solids or liquids. Examination of Figure 10 reveals two temperature arrests. The top curve, for metal, exhibits a temperature arrest just above 1093° C (2000° F), which is the freezing point of the metal. Once the metal is frozen the temperature declines further. The sand temperature (other curves in Figure 10) exhibits an arrest at 100° C (212° F) 2.5 cm (1 in.) from the metal surface. This temperature is the boiling point of water and represents the drying of the sand-clay-water mixture. Unfortunately, data are not available for sand temperatures at distances greater than 1 in. from the metal surface, but thermodynamic principles predict that at greater distances the 100° C (212° F) thermal arrest will last longer and at even further distances it will dictate the maximum achievable temperature. Therefore, in large molds there is considerable amount of material available as a condensing receiver for pyrolysis products. The pyrolysis products will condense and be "stored" on the cooler sand surrounding the metal, as discussed in Section 9.

When the mold is shaken out and the cooler sand comes into contact with the warmer sand and metal, condensed pyrolysis products will be boiled off, forming a second emission.

In one laboratory study, the quantity of gases involved from a no-bake core was investigated at various temperatures. Figure 11 shows the results for a phenol-formaldehyde resin and a toluene sulfonic acid catalyst.[30] A molding sand containing both Western and Southern bentonite as well as seacoal was tested at 1010° C (1850° F) and emitted gas as shown by the top curve of Figure 12.[30] Although base sands are not generally considered as emission sources, small quantities of gas were evolved from Illinois silica sand ($\cong 1$ cm^3/g) and silica sand mixed with dolomite ($\cong 7$ cm^3/g) at 1010° C (1850° F) during laboratory experiments.[30] The only quantitative literature data available on organic emissions was that of Bates and Scott.[21] In tests with green sand molds they found total hydrocarbons to peak at 1200 ppm after pouring and 1500 ppm after shakeout. On the other hand, the time average emissions reported for hydrocarbons was 1780 ppm for pouring and 640 ppm for shakeout.

6.5 DECOMPOSITION PRODUCTS OF SUBSTANCES USED IN MOLDS AND CORES

Moldmaking involves the use of organic and inorganic chemical additives. These substances can pyrolyze or decompose during use of the mold. The decomposition products may react to produce further products. The high temperature that these products may attain and their exposure to oxygen in the exit gases are important in determining the final pollutant composition in any particular case.

Most binders are blends of several substances that, together meet desired processing characteristics. Many formulations are proprietary,

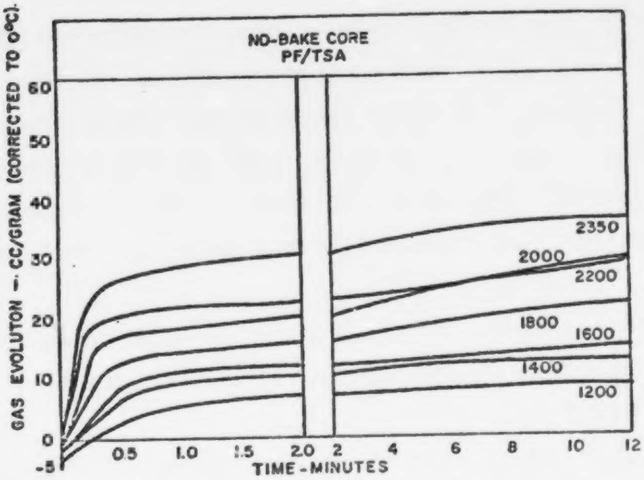


Figure 11. Quantity of gases evolved from a phenol-formaldehyde no-bake core at various temperatures (in °F)[30] (reprinted from AFS Transactions, 1976).

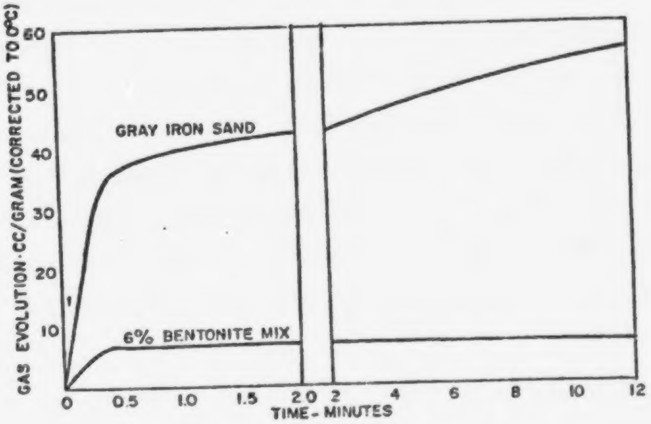


Figure 12. Evolution of gases from molding sands[30] (reprinted from AFS Transactions, 1976)

nevertheless some 46 substances are reported as components of currently used binders (including complex mixtures such as pitch).

A study was made of the chemical literature to determine the known pyrolysis products from chemicals used in moldmaking. Appendix A is a complete listing of the findings of this study. A listing of the pyrolysis products expected from the resins used by the foundries sampled is given in Table 15.

TABLE 15. PYROLYSIS PRODUCTS OF SOME BINDER MATERIALS

Substance	Decomposition Products
Phenol-Formaldehyde	At 620° C: Carbon monoxide and dioxide
	Hydrogen
	Methane
	Phenol
	Formaldehyde
	Ammonia
	Hydrogen cyanide[53,54]
	Acetylene
	Ethylene
	Ethane[55]
Phenolic Resins (Novalak and Resole)	Same as phenol-formaldehyde plus:
	Allene
	Methylacetylene
	Propylene
	Acetaldehyde
	Methyl chloride
	Acrolein
	Acetone
	Propionaldehyde
	Vinyl chloride
	Ethyl chloride
	Cyclopentadiene

(continued)

TABLE 15. (cont'd)

Substance	Decomposition Products
Phenolic Resins (continued)	Benzene
	Methylcyclopentadiene
	Toluene
	Cresols
	Methylenediphenol
	C_2 phenols
	Ethylene diphenol
	C_3H_2 phenol
	Propene[56]
Phenol Urethane	Acetylene
	Carbon monoxide and dioxide
	Ethane
	Ethylene
	Hydrogen
	Methane
	The nitrogen in the isocyanate should yield:57 Ammonia Simple amines Aniline Hydrogen cyanide
	The phenolic component should produce: Formaldehyde Substituted phenols

7.0 ENVIRONMENTAL DATA ACQUISITION

Reviewing the literature on the environmental aspects of foundries reveals incomplete evaluation of the emission of organic chemicals by chemical binders, although laboratory studies have been performed verifying that a potential problem exists.[21]

7.1 SAMPLING AND ANALYTICAL STRATEGY

Two decisions were made prior to performing environmental tests at a foundry, namely; which operation to test and which chemical formulation to test. Discussions with the American Foundrymen's Society, and the study presented in Section 6.5 identified five process areas and five molding systems as candidates for environmental sampling. The process areas are pouring and cooling, shakeout, return sand belts, coke ovens, and hot box and shell coke making. The chemical formulations of concern are seacoal, isocyanate, phenol-formaldehyde, polyphosphate esters, and polystyrene as used in the Full Mold® system.

Considering the large quantity of pollutants estimated to be produced from shakeout, the relative ease of sampling and sampling cost, the shakeout was selected as a suitable site for measuring organic emissions.

The phenolic-isocyanate and seacoal systems were selected due to their common use and potential for pollution. This was pursued by sampling an operation that used phenolic-isocyanate cores in green sand molds with seacoal added. The second system selected was a shell molding foundry using phenol-formaldehyde binder.

The philosophy of the phased approach developed by the Process Measurements Branch of the Industrial Environmental Research Laboratory at Research Triangle Park, N.C. was employed as a guide in the sampling and analysis. The Level 1 Procedure Manual outlines this approach and describes the Level 1 sampling and analytical techniques. The goal of Level 1 sampling and analysis is to identify the pollution potential of a source in a quantitative manner within a factor of ±2 to 3. This does not require a statistically representative sample. The sample is acquired with the Source Assessment Sampling System which collects particulates by size range and removes organic and inorganic vapors from the air.

A more sensitive although not comprehensive analysis was planned if the Level 1 analysis indicated possible PNA compounds, which did occur. Otherwise the analytical techniques were as described in the Level 1 manual.

7.2 TEST SITE SELECTION

The selection of sampling sites was based on the binders used, the level of air pollution control employed, and permission to sample. The AFS suggested possible sites and the companies contacted were cooperative and friendly. The preferred sample site experienced a change in level of operation which necessitated replanning and selection of an alternate site. Two foundries were selected.

Foundry A is a large modern installation producing ductile iron castings. After melting, the iron is desulfurized, then inoculated by the magnesium plunging technique, and transferred to the pouring ladles.

The molding lines are automated, producing a mold every 12 seconds on each line. The green sand drags are fitted with phenolic isocyanate cores prior to placement of the copes. After pouring the molds make a 47 minute tour of the cooling room and are then "punched out" onto a vibrating grate to separate the sand from the castings. The "punch out" shakeout operation (hereafter referred to as shakeout) is completely enclosed and air is drawn through it by a 32 inch duct to a 30,000 cfm wet Ventri-Rod^{TM} scrubber made by Riley Environeering Inc. Three independent scrubber systems are used on each molding line, with one dedicated to the shake out. Figure 13 shows the general nature of the structure and the sample points. Samples one and two were obtained at Foundry A.

Foundry B is a shell molding foundry using phenol formaldehdye bound sand shells mounted in boxes and surrounded with iron shot. The foundry has virtually no free floor space except a minimum amount for fork lift trucks to transport materials. The air control system is mostly general ventilation. The shakeout room is a large room in which the railcars are inverted 135°, dumping the contents onto a shakeout table. Exhaust fans are located

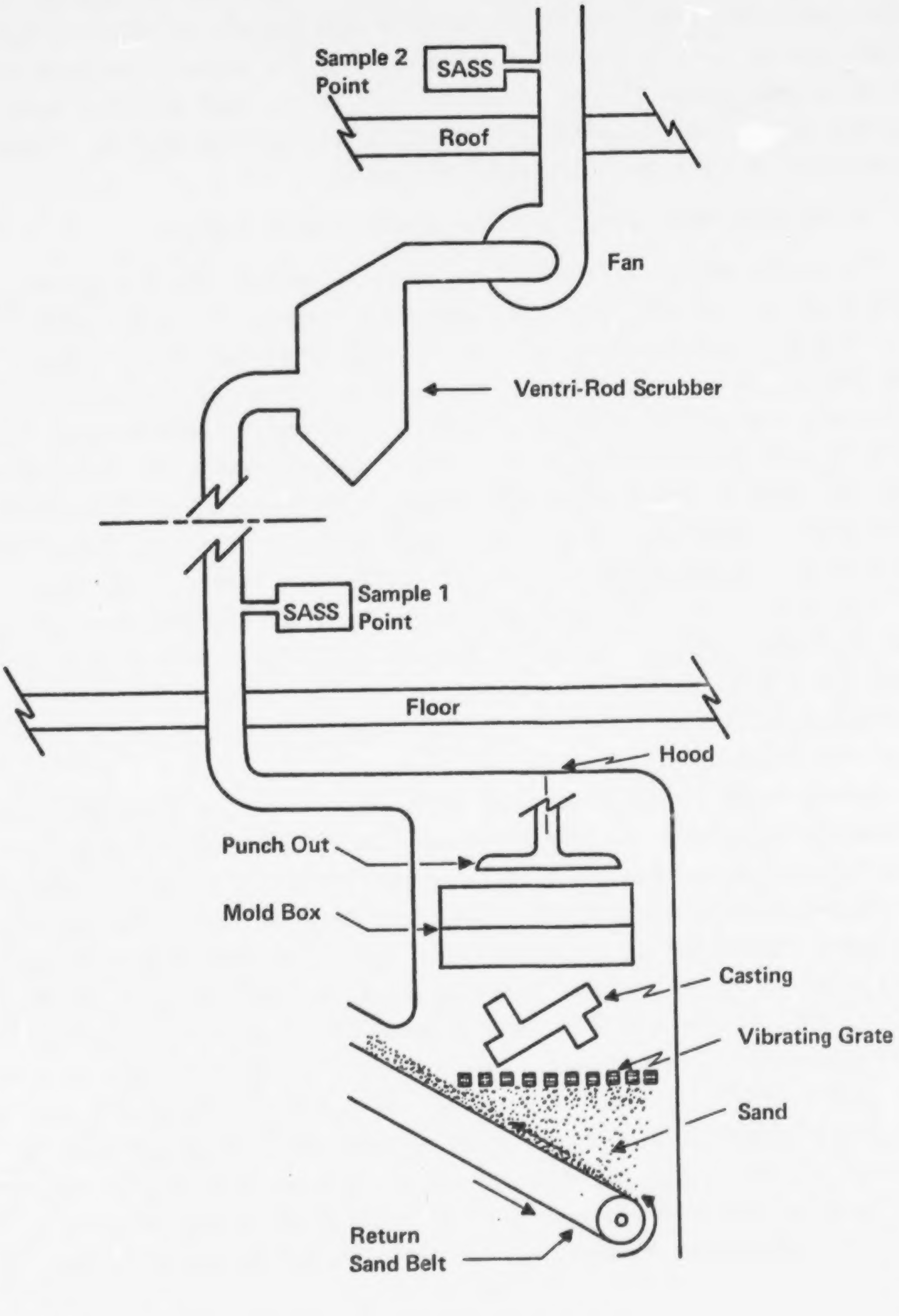

Sample 2
Point
SASS
Roof
Fan
Ventri-Rod Scrubber
SASS
Sample 1
Point
Floor
Hood
Punch Out
Mold Box
Casting
Vibrating Grate
Sand
Return
Sand Belt

Figure 13. Sampling of Shake-out Emissions.

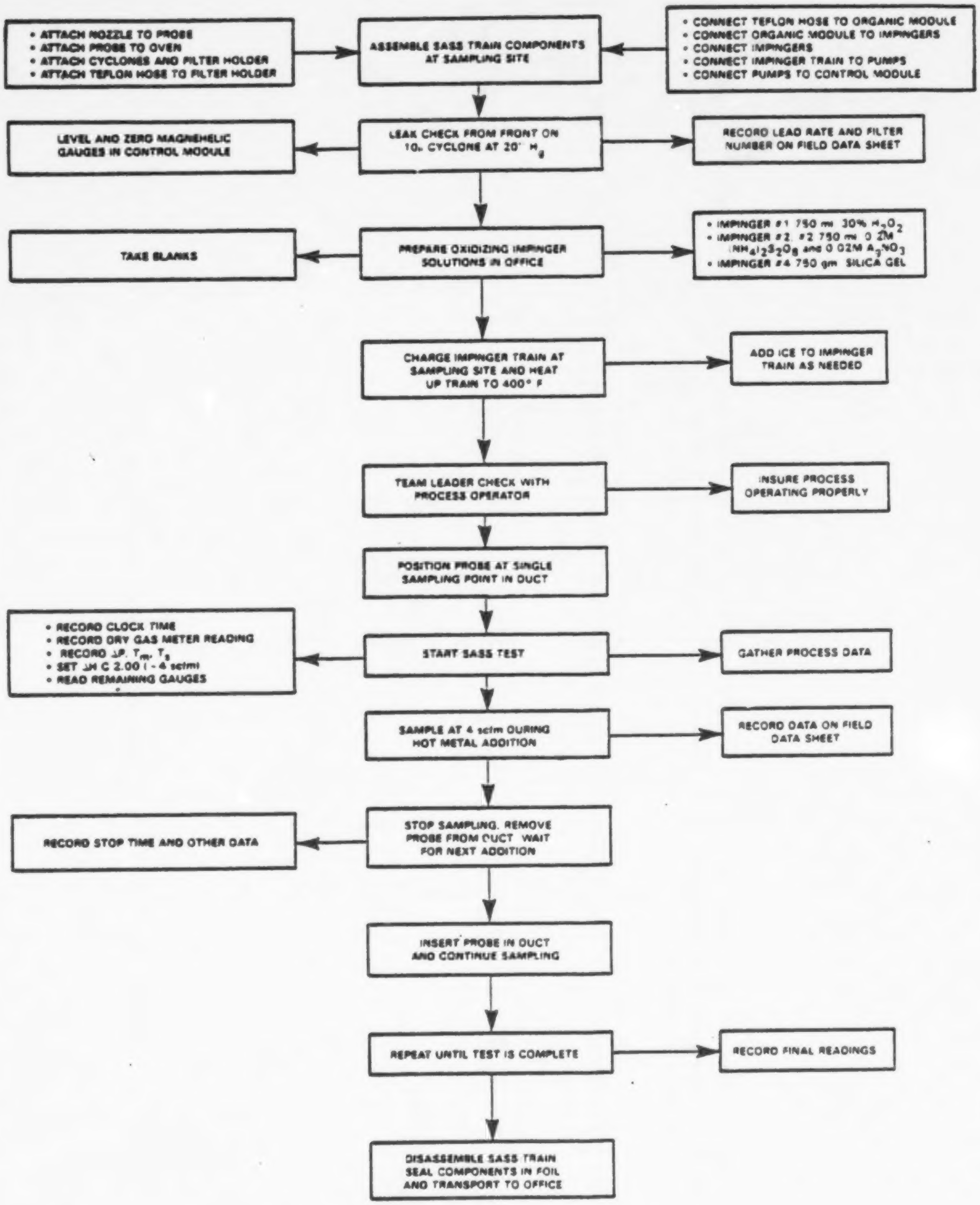
at a considerable elevation in the room's wall and are essentially inaccessible for sampling purposes. The room has an open door and the emitted smoke occasionally took that exit. Fugitive sampling was all that could be accomplished at that location, but the density of the smoke in the room was such as to make observation of the process difficult, leading to the conclusion that a reasonable quantity of organic vapors could be obtained. Sample 3 was obtained in the shake out room of Foundry B.

7.3 SOURCE ASSESSMENT SAMPLING SYSTEM ACQUISITION OF SAMPLES

The sample were acquired with the Source Assessment Sampling System, commonly called the SASS train, built by Acurex Corporation. This unit draws in air through a nozzle, at a velocity matching that of the stream being sampled, and conveys it via a heated tube to a series of three cyclones in an oven. The cyclones separate the >10μ, >3μ, and >1μ particulates. The sample is then passed through a fiberglass filter to remove the <1μ particulates, and then is cooled and passed through a cartridge of XAD-2 resin to adsorb organic materials. After the organic vapors are removed, the collected air passes through a series of reagent bubblers to remove inorganics.

All reagents and procedures were according to the recommended practices found PB-257850, IERL-RTP Procedures Manual Level 1 Environmental Assessment except that a NaOH bubbler was used for determining cyanide. Figure 14 is the flow scheme showing steps taken in the sampling procedure, and Figures 15 and 16 show the sample recovery procedures.

Foundry A had pre-existing ports on the roof stacks for the SASS probe. The company installed ports in a duct drawing air from the shakeout hood to enable traverse measurements and sampling upstream of the scrubber. Obtaining the proper distance downstream from a bend resulted in the sampling probe being located 8 feet above the floor. Figure 13 shows the sampling points relative to the process. Sampling was at a single point in the ducts at a flow rate through the SASS train of about 0.11 scmm (4 scfm) to insure proper operation of the cyclones. The sampling probe and oven were maintained at 121° C (250° F) instead of the usual 204° C (400° F) because it was known that the particulates probably contain coal dust and carbonaceous petroleum residues, which would distill volatile organics at higher temperatures, thereby biasing the measurements of organic vapors emitted. The production records were obtained, giving full information on metal, sand,



• ATTACH NOZZLE TO PROBE
• ATTACH PROBE TO OVEN
• ATTACH CYCLONES AND FILTER HOLDER
• ATTACH TEFLON HOSE TO FILTER HOLDER
ASSEMBLE SASS TRAIN COMPONENTS AT SAMPLING SITE
• CONNECT TEFLON HOSE TO ORGANIC MODULE
• CONNECT ORGANIC MODULE TO IMPINGERS
• CONNECT IMPINGERS
• CONNECT IMPINGER TRAIN TO PUMPS
• CONNECT PUMPS TO CONTROL MODULE
LEVEL AND ZERO MAGNEHELIC GAUGES IN CONTROL MODULE
LEAK CHECK FROM FRONT ON 10μ CYCLONE AT 20" Hg
RECORD LEAD RATE AND FILTER NUMBER ON FIELD DATA SHEET
TAKE BLANKS
PREPARE OXIDIZING IMPINGER SOLUTIONS IN OFFICE
• IMPINGER #1 750 ml 30% H_2O_2
• IMPINGER #2, #2 750 ml 0.2M $(NH_4)_2S_2O_8$ and 0.02M A_gNO_3
• IMPINGER #4 750 gm SILICA GEL
CHARGE IMPINGER TRAIN AT SAMPLING SITE AND HEAT UP TRAIN TO 400° F
ADD ICE TO IMPINGER TRAIN AS NEEDED
TEAM LEADER CHECK WITH PROCESS OPERATOR
INSURE PROCESS OPERATING PROPERLY
POSITION PROBE AT SINGLE SAMPLING POINT IN DUCT
• RECORD CLOCK TIME
• RECORD DRY GAS METER READING
• RECORD ΔP, T_m, T_s
• SET ΔH C 2.00 (- 4 scfm)
• READ REMAINING GAUGES
START SASS TEST
GATHER PROCESS DATA
SAMPLE AT 4 scfm DURING HOT METAL ADDITION
RECORD DATA ON FIELD DATA SHEET
RECORD STOP TIME AND OTHER DATA
STOP SAMPLING. REMOVE PROBE FROM DUCT. WAIT FOR NEXT ADDITION
INSERT PROBE IN DUCT AND CONTINUE SAMPLING
REPEAT UNTIL TEST IS COMPLETE
RECORD FINAL READINGS
DISASSEMBLE SASS TRAIN SEAL COMPONENTS IN FOIL AND TRANSPORT TO OFFICE

Figure 14. SASS train sampling procedures.

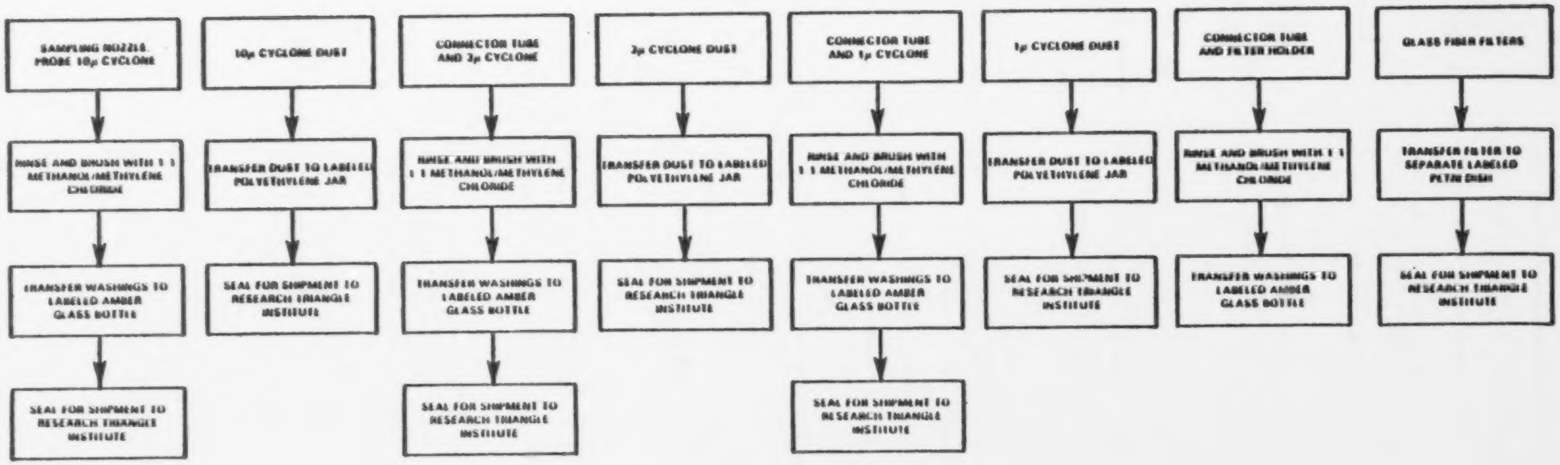
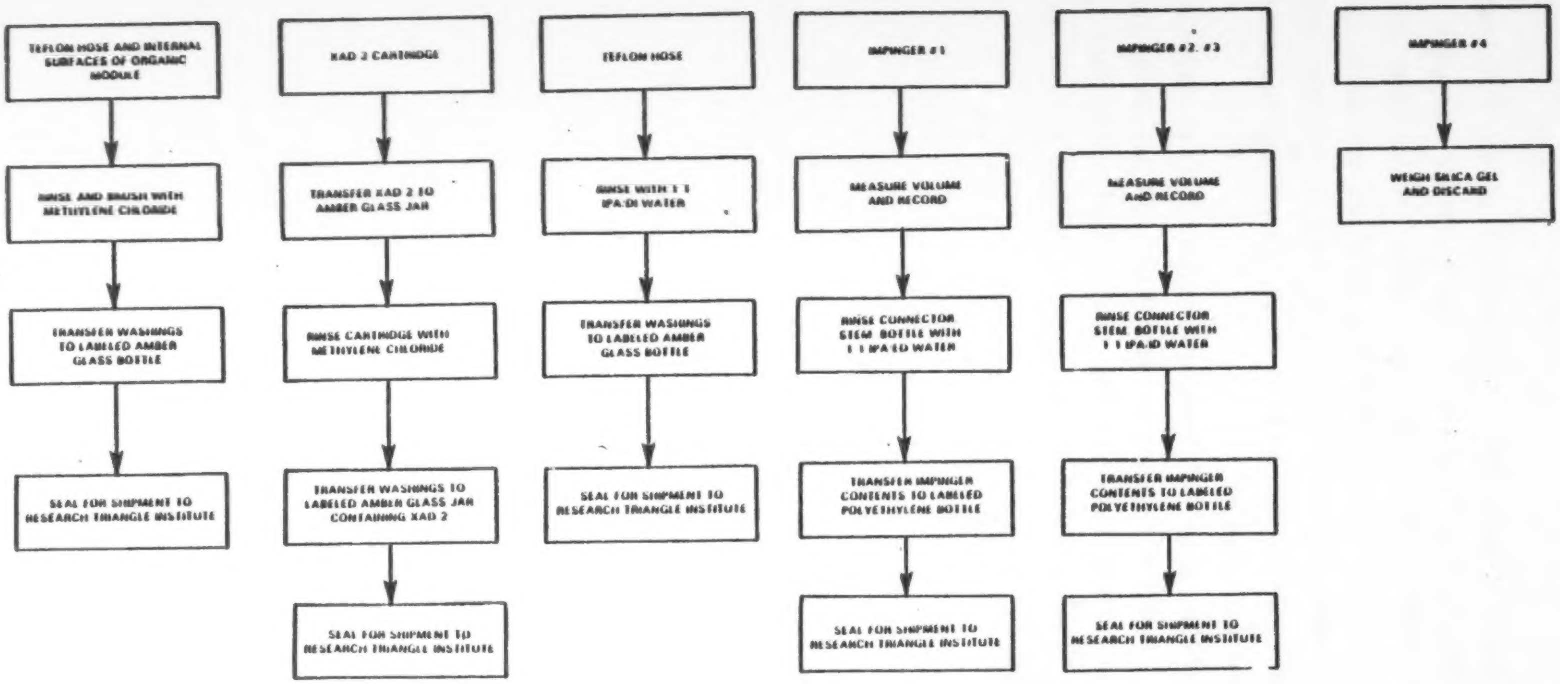

SAMPLING NOZZLE, PROBE 10μ CYCLONE
RINSE AND BRUSH WITH 1:1 METHANOL/METHYLENE CHLORIDE
TRANSFER WASHINGS TO LABELED AMBER GLASS BOTTLE
SEAL FOR SHIPMENT TO RESEARCH TRIANGLE INSTITUTE
10μ CYCLONE DUST
TRANSFER DUST TO LABELED POLYETHYLENE JAR
SEAL FOR SHIPMENT TO RESEARCH TRIANGLE INSTITUTE
CONNECTOR TUBE AND 3μ CYCLONE
RINSE AND BRUSH WITH 1:1 METHANOL/METHYLENE CHLORIDE
TRANSFER WASHINGS TO LABELED AMBER GLASS BOTTLE
SEAL FOR SHIPMENT TO RESEARCH TRIANGLE INSTITUTE
3μ CYCLONE DUST
TRANSFER DUST TO LABELED POLYETHYLENE JAR
SEAL FOR SHIPMENT TO RESEARCH TRIANGLE INSTITUTE
CONNECTOR TUBE AND 1μ CYCLONE
RINSE AND BRUSH WITH 1:1 METHANOL/METHYLENE CHLORIDE
TRANSFER WASHINGS TO LABELED AMBER GLASS BOTTLE
SEAL FOR SHIPMENT TO RESEARCH TRIANGLE INSTITUTE
1μ CYCLONE DUST
TRANSFER DUST TO LABELED POLYETHYLENE JAR
SEAL FOR SHIPMENT TO RESEARCH TRIANGLE INSTITUTE
CONNECTOR TUBE AND FILTER HOLDER
RINSE AND BRUSH WITH 1:1 METHANOL/METHYLENE CHLORIDE
TRANSFER WASHINGS TO LABELED AMBER GLASS BOTTLE
GLASS FIBER FILTERS
TRANSFER FILTER TO SEPARATE LABELED PETRI DISH
SEAL FOR SHIPMENT TO RESEARCH TRIANGLE INSTITUTE

Figure 15. SASS train sample recovery procedures.


TEFLON HOSE AND INTERNAL SURFACES OF ORGANIC MODULE
RINSE AND BRUSH WITH METHYLENE CHLORIDE
TRANSFER WASHINGS TO LABELED AMBER GLASS BOTTLE
SEAL FOR SHIPMENT TO RESEARCH TRIANGLE INSTITUTE
XAD 2 CARTRIDGE
TRANSFER XAD 2 TO AMBER GLASS JAR
RINSE CARTRIDGE WITH METHYLENE CHLORIDE
TRANSFER WASHINGS TO LABELED AMBER GLASS JAR CONTAINING XAD 2
SEAL FOR SHIPMENT TO RESEARCH TRIANGLE INSTITUTE
TEFLON HOSE
RINSE WITH 1:1 IPA:DI WATER
TRANSFER WASHINGS TO LABELED AMBER GLASS BOTTLE
SEAL FOR SHIPMENT TO RESEARCH TRIANGLE INSTITUTE
IMPINGER #1
MEASURE VOLUME AND RECORD
RINSE CONNECTOR STEM BOTTLE WITH 1:1 IPA:DI WATER
TRANSFER IMPINGER CONTENTS TO LABELED POLYETHYLENE BOTTLE
SEAL FOR SHIPMENT TO RESEARCH TRIANGLE INSTITUTE
IMPINGER #2, #3
MEASURE VOLUME AND RECORD
RINSE CONNECTOR STEM BOTTLE WITH 1:1 IPA:DI WATER
TRANSFER IMPINGER CONTENTS TO LABELED POLYETHYLENE BOTTLE
SEAL FOR SHIPMENT TO RESEARCH TRIANGLE INSTITUTE
IMPINGER #4
WEIGH SILICA GEL AND DISCARD

*NO CONDENSATE COLLECTED IN GLASS CONDENSATE JAR

Figure 16. SASS train sample recovery procedures.

and cores on an hourly basis except when the line went down. Full records were available on a minute by minute basis of work stoppage and work accomplished. These were provided by the companies. When the scrubber outlet was sampled, the water flow and operation of the scrubber was continuously monitored to insure that sampling only occurred while the scrubber was operating. Likewise, periodic checks were made of the production line, but the down-time was for pattern changes.

Foundry B had a shakeout room which was evacuated by inaccessible fans at the top of the room. Considerable smoke emanated from the shakeout and no flow pattern of air was discernable at the floor level. The SASS train was used with only the filter and XAD-2 cartridge to obtain a fugitive sample about 10 feet from the shakeout.

8.0 ENVIRONMENTAL DATA ANALYSIS

Three samples were collected using the SASS train. Tables 16 and 17 summarize the results of particulate and organic data obtained for the three samples. The source of the samples is detailed below.

TABLE 16. SUMMARY OF PARTICULATE DATA

Sampling Site	Sample 1 Green sand shakeout before scrubber	Sample 2 Scrubber outlet	Sample 3 Shell mold shakeout
Air flowrate m^3/min	635	867	(fugitive)
Particulate concentration, mg/m^3	1,996	8.92	49.59
Particulate generated kg/tonne cast	7.01	0.0434	-

TABLE 17. SUMMARY OF ORGANIC DATA

Sampling Site	Sample 1 Green sand shakeout before scrubber	Sample 2 Scrubber outlet	Sample 3 Shell mold shakeout
Air flow rate, m^3/min	635	857	-
Total organic concentration mg/m^3	174.61	105.3	29.7
Total organic generated, kg/tonne cast	0.614	0.512	-

TABLE 18. PRODUCTION DURING SAMPLING

	Sample 1	Sample 2	Sample 3
Total metal, tonnes	27.841	59.809	25.445
Metal/hr, tonnes	10.789	10.556	15.118
Total cores, tonnes	9.945	18.678	-
Total sand, tonnes	114.519	279.682	-
Total sand + cores, tonnes	124.464	298.359	-
(Sand + core)/metal ratio	4.471	4.989	0.0365
Sample volume, m^3	15.23	26.15	12.47
Air flow/ton cast:	3,516m^3	4,865m^3	-
Shell + cores, tonnes	-	-	9.285
Shot, tonnes	-	-	262.529

Table 18 summarizes the production data during the sampling periods. The stack and SASS train data are listed in the Appendix.

Production and material data pertinent to samples 1 and 2 are as follows:

Normal casting rate: 11-17 tonnes per hour
Weight of iron per mold: 63.6-72.7 kg (140 to 160 lbs)
Weight of individual pieces: about 4.1 kgs (9 lbs)
Maximum rate of casting: 250 molds/hour
Minimum cooling time: 47 minutes
Weight of green sand per mold: 340-364 kg (750-800 lb)
Weight of cores per mold: 18-23 kg (40-50 lbs)
Sand to metal ratio: 5:1
Percentage core sand: 6%
Size of molds: 61 × 81 × 41 cm (24" × 32" × 16")
Temperature of fresh return sand: 121-177° C (250-350° F)
Temperature of cooled return sand: 30.7° C (97.2° F ± 2.5)
Carbon content of return sand: 1.16 ± 0.15%
Moisture in molding sand: 2.96 ± 0.36%
Analysis of green sand:

New sand: 5%, Compression Strength: 20 psi

Clay: 7.5% (bentonite)

Water: 3.0%

Combustibles: 4.0%

Volatiles (at 482° C): 2.0% (1.9% during test)

Organic components:

"Charbo" - charred oat hulls

"Kleankast"-Asphalt Emulsion.

(Due to changeover from seacoal to kleankast, the noncharbo organic content was 70% seacoal (0.57% of sand), 30% kleankast).

Analysis of Cores:

Percent binder: 1.75%

Composition of binder:

315 Phenolic 0.9625%

615 Isocyanate 0.7875%

Catalyst: TEA 0.10%-0.20% of Sand Weight

Density: 95 lbs/cu. ft.

Tensile Strength: 100-200 psi.

Sand: Lake; 50 GFN; ADV 0-5

The collected samples were subjected to analysis by the following procedure outline:

Organic Vapors collected by XAD-2 resin and rinses of SASS train:

Soxhlet Extraction
TCO and Gravimetry
LC; IR; LRMS; TCO; GRAV

Particulates collected in cyclones and filter:

Gravimetry
Soxhlet Extraction
Parr/Acid Digestion
SSMS
As/Hg/Sb

NaOH Impinger:

CN^- analysis.

Further, a portion of the organic extract of the XAD-2 was subjected to GC-MS analysis.

Sample 1

This is the "master sample" the uncontrolled effluent from shakeout. The molding line was using phenolic isocyanate bound cores in green sand molds with seacoal and "kleankast"® additions.

This sample was taken from a duct on the floor above the shakeout hood as shown in Figure 13 by standard SASS train procedures. The air flow in the duct was 10.526cm^3/sec, which was 3,516 m^3/tonne of metal cast during the sample period.

Sample 2

This sample came from the same source and conditions as sample 1 with the difference that it was obtained after the air had passed through a wet scrubber. This sample was obtained the day following sample 1. This sample is the controlled atmosphere discharge. During the collection of sample 2, the air flow was 4,865 m^3/tonne of metal cast, at a rate of 14.375 m^3/sec.

This flow is greater than for sample 1. The only observable reason for this is the presence of leaks in the system. The air is drawn by suction from the shakeout hood up through the wet scrubber. The air ducts had been damaged by erosion--corrosion, and other factors. The damage was between the take off duct from the shakeout hood and the scrubber, allowing ambient air from above the casting line to enter the system.

Sample 3

Sample 3 was taken in a room in which phenol-formaldehyde shell molds were dumped onto a shakeout table. The shells were held in flasks and surrounded with iron shot for the casting operation. The process weight during the test was 194.66 tons/hour, consisting of 6.08 tons/hr shells and cores, 16.65 tons/hr iron poured, and 171.82 tons/hr of supporting shot.

The shot temperature was 232° C (450° F).

8.1 ANALYSIS OF SASS TRAIN SAMPLING OF GREEN SAND SHAKEOUT EFFLUENT; SAMPLE 1

Sample 1 is the shakeout effluent from green sand molds containing phenolic isocyanate cores. Both seacoal and petroleum additives were used in the green sand. The importance of this sample is that it represents a typical casting operation and the environmental emissions before any air pollution control efforts are made.

TABLE 19. PARTICULATE CONCENTRATION

Sample: 1, Shakeout, Green sand, Line 5

Category	Weight, mg	Load, mg/m^3	Total Emission, g/tonne cast
<1μ dust	83.2	5.46	19.2
1-3μ dust	925.1	60.74	213.6
3-10μ dust	3,740.4	245.59	863.5
>10μ dust	25,447.0	1,670.85	5,874.7
Probe rinse	196.1	12.88	45.28
Total	30,3918	1,995.5	7,017

Sample volume at 15.5° C and 76.1 cm Hg: 15.23m^3

Total load in grains/ft^3: 0.8720

Metal cast during sample period: 27.841 tonnes

Air flow/tonne cast: 3,516m^3 (Std. dry)

8.1.1 Total Particulate Loading

The total mass of particulates from an uncontrolled shakeout is given in Table 19. Included in this table are the values of particulate emission per ton of metal cast. Since the sand to metal ratio was 5:1, a common target value, these values could be extrapolated to obtain an order of magnitude estimate for similar plants. It should be noted that particulates would be emitted even if the production line was operating temporarily without iron being poured, since shaking out molds containing no iron will still produce dust. The quantity of fine particles would probably be smaller in that case. Table 20 summarizes the sampling conditions.

8.1.2 Level 1 Organic Analysis

Table 21 presents the organic extractables. The distribution among the sizes of the particulates might be correlated with the fact that the larger particles are likely to be made up of coal dust and carbonized petroleum additive, which contain significant amounts of organic material. The fine particulates were probably clay, as indicated by the inorganic analysis. The organics in the vapor phase were 94.3 percent TCO material, that is, low boiling and smaller molecules.

TABLE 20. SUMMARY OF SAMPLING DATA FOR GREEN SAND SHAKEOUT, SAMPLE NO. 1

Date of test:	6/28/78
Volume of gas sampled: 15.23m^3	(537.81 dscf)
Duct gas temperature: 68.9° C	(156° F)
Duct gas pressure: 75.95cm	(29.90 inches Hg)
Duct gas molecular weight:	28.84
Duct gas moisture:	3%
Duct gas velocity: 15.46m/sec	(50.72 ft/sec.)
Duct gas flowrate: 10.53m^3/sec	(22,304 dscfm)
Total sampling time: 9300 sec	(155 minutes)
SASS train flowrate: 0.001638m^3/sec	(3.47 dscfm)
Iron cast during sampling: 27.841 tonnes	(30.667 tons)

TABLE 21. ORGANIC EXTRACTABLES, SAMPLE 1

Type of Sample	Emission conc. mg/m^3	Emission conc. g/tonne cast
Filter: (>1μ)	0	0
>3μ:	0.12	0.42
>10μ:	0.82	1.32
XAD-2:	173.67*	610
Total	174.61	612

*94.3% TCO

Table 22 summarizes the LC and IR analysis of the vapor phase organics collected by the XAD resin. The detailed summary by LC fractions is found in the Appendix.

TABLE 22. SUMMARY OF ORGANIC VAPOR ANALYSIS FROM GREEN SAND SHAKEOUT, SAMPLE 1.
Emission rate: 554 g/ton cast

Category	Found mg/m^3	Min. MATE value in category mg/m^3	Ratio $\frac{\text{conc. found}}{\text{MATE}}$
Aliphatics	0.72	20	0.04
Haloaliphatics	0.22	0.1	2.2
Substituted benzenes	2.45	1.0	2.45
Halobenzenes	0.24	0.7	0.34
Fused aromatics	2.45	0.001 to 200	24,000
Hetero N compounds	0.56	0.1	5.6
Hetero O compounds	0.10	300	0.00
Hetero S compounds	0.10	2	0.05
Alkyl S compounds	0.06	1	0.06
Nitriles	0.01	1.8	0.01
Aldehydes, ketones	0.10	0.25	0.4
Nitroaromatics	0.01	1.3	0.01
Ethers, Epoxides	0.10	16	0.01
Alcohols	0.56	10	0.06
Phenols	0.56	2	0.28
Amines	0.56	0.1	5.60
Amides	0.47	1.0	0.47
Esters	0.15	5.0	0.03
Carboxylic acids	0.46	0.3	1.53
Sulfonic acids	0.05	0.8	0.06
GRAV conc.	9.85		
TCO conc.	163.8		

The MATE values are the Minimum Acute Toxicity of Effluent values, or the minimum quantity that has been determined to be detrimental to the environment. These are "Air, Health MATE" values from the "MEGs" or Multimedia Environmental Goals[91]. The MEGS give a MATE value for each individual compound. The values listed in this report are the lowest MATE values in each category of compounds. Thus, unless the specific compound having this MATE value is actually in the sample, the MATE value shown would be too low and the concern ratio too high.

The LRMS data (Appendix) indicated possible PNA's. The sample was analyzed by GC-MS for confirmation. Known compounds, listed in Table 23, were introduced to the GC-MS to obtain calibration factors, which were then used to quantify the same compounds in the sample. The results in Table 23 show that the concentration of PNA tested for are well below the MATE values. The highest concentration found (for naphthalene) is only 3 percent of the MATE value. The GC-MS system used can identify PNA's with molecular weights below about 270. No PNA's between 229 and 270 (which includes benzo(a)pyrene) were found. Since BaP and the high molecular weight PNA's are from the same source (the shakeout) as the PNA's tested for, the low values found by GC-MS analysis indicate an equal or lower concentration of the higher molecular weight PNA's. The identity of the fused aromatics indicated by LRMS and not listed in Table 23 is not known. If the Level 1 analysis is correct, then 1/3 of the fused aromatics are unaccounted for, by GC-MS. However, the technique used by Level 1 procedures is too inaccurate to firmly establish the quantitative level.

The GC-MS analysis produced a complete set of mass spectra for each GC peak. Figure 17 is the gas chromatogram of sample one. The 21 chromatographic peaks that exceeded 9.6% of the highest concentration components, (β-methylene naphthalene and an unsaturated C_6 akyl benzene isomer) were interpreted. Table 24 lists the substances identified along with the relative peak heights of the 21 peaks analyzed. The peak height is proportional to concentration and can therefore be used to measure relative concentrations to a first approximation. (Accurate determinations require comparison with a known quantity of the substance of concern.) By summing all peak heights it was estimated that the 21 peaks analyzed represent 79% of the total quantity of material analyzed. 62 peaks (representing 21% of the material)

TABLE 23. QUANTITATIVE DETERMINATION OF PNA COMPOUNDS PRESENT IN GREEN SAND SHAKEOUT, SAMPLE 1

Compound	MW	ng/μl	Wt. in total extract (μg)	Conc. $\mu g/m^3$	Air health mate $\mu g/m^3$
Naphthalene	128	452.0	22,600	1,484	50,000
Dibenzofuran	168	3.0	150	9.8	N
Anthracene	178	11.2	560	36.8	56,000
Phenanthrene	178	2.3	115	7.6	1,600
Fluoranthene	202	0.2	10	0.7	90,000
Pyrene	202	0.2	10	0.7	230,000
Chrysene	228	4.7	235	15.4	2,200
Total				1,555 mg/m^3	

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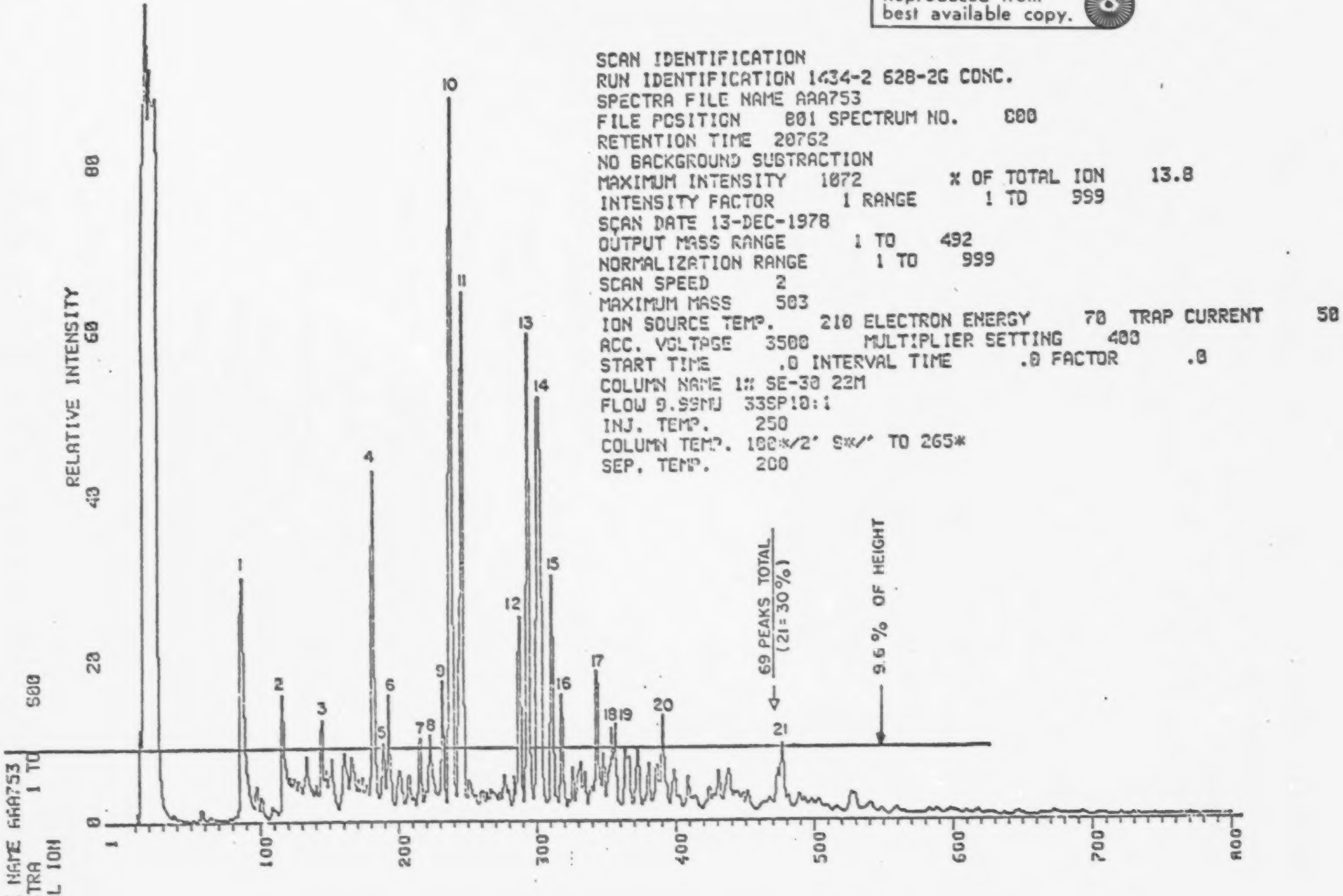

```
SCAN IDENTIFICATION
RUN IDENTIFICATION 1434-2 628-2G CONC.
SPECTRA FILE NAME AAA753
FILE POSITION    801 SPECTRUM NO.    000
RETENTION TIME  20762
NO BACKGROUND SUBTRACTION
MAXIMUM INTENSITY   1072        % OF TOTAL ION    13.8
INTENSITY FACTOR      1 RANGE      1 TO    999
SCAN DATE 13-DEC-1978
OUTPUT MASS RANGE       1 TO    492
NORMALIZATION RANGE       1 TO    999
SCAN SPEED       2
MAXIMUM MASS     503
ION SOURCE TEMP.    210 ELECTRON ENERGY     70  TRAP CURRENT     50
ACC. VOLTAGE   3500     MULTIPLIER SETTING    400
START TIME      .0 INTERVAL TIME      .0 FACTOR     .0
COLUMN NAME 1% SE-30 22M
FLOW 9.99MJ  33SP10:1
INJ. TEMP.    250
COLUMN TEMP. 100*/2' 8*/' TO 265*
SEP. TEMP.    200
```

RELATIVE INTENSITY
0
20
40
60
80
FILE NAME AAA753
SPECTRA 1 TO 500
TOTAL ION
1
100
200
300
400
500
600
700
800
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
69 PEAKS TOTAL
(21 = 30%)
9.6 % OF HEIGHT

Figure 17. Gas chromatogram of organic effluents, sample 1.

TABLE 24. IDENTITIES OF MAJOR ORGANIC COMPONENTS IN AIR SAMPLE 1

Chromatographic peak no.	Relative peak height	Percent of sample	Compound
1	.34	4.2	Aniline
2	.18	2.2	Phenol
3	.14	1.7	Cresol isomer
4	.49	6.0	$C_{11}H_{24}$ isomer
5	.11	1.3	Naphthalene
6	.18	2.2	C_5-alkylbenzene isomer $C_{12}H_{26}$ isomer
7	.12	1.4	Dimethylindan isomer
8	.12	1.5	Dimethylindan isomer C_6 alkylbenzene isomer
9	.19	2.4	C_6 alkylbenzene isomer $C_{14}H_{30}$ isomer Dimethylindan isomer
10	1.00	12.3	β-methylnaphthalene Unsaturated C_6 alkylbenzene isomer C_6 alkylbenzene isomer
11	.73	9.1	$C_{13}H_{28}$ isomer α-methylnaphthalene
12	.28	3.5	Ethylnapthalene isomer Trimethylindan isomer
13	.68	8.3	Ethylnaphthalene isomer $C_{14}H_{30}$ isomer
14	.59	7.2	Dimethylnaphthalene isomer Diphenylmethane
15	.34	4.2	Dimethylnaphthalene isomer
16	.18	2.2	Dimethylnaphthalene isomer
17	.21	2.6	$C_{15}H_{32}$ isomer C_3 alkylnaphthalene isomer
18	.13	1.6	C_3 alkylnaphthalene isomer
19	.14	1.7	C_3 alkylnaphthalene isomer
20	.15	1.8	$C_{16}H_{34}$ isomer Di-p-tolymethane (tent.)
21	.11	1.3	$C_{17}H$ isomer Anthracene-d_{10}

were not analyzed. Table 24 also lists the percentage of each substance in the sample. This is based on the assumption that equal quantities of any substance produce equal peak heights, which is not true, therefore these values are an approximation for comparison only. The GC spectrum is presented in the appendix as Figure A1. The 36 predominant compounds in the sample were identified. Nine are benzene compounds, 18 are two ring polycyclics, 11 of which are naphthalenic compounds, and one, anthracene, is a 3 ring polycyclic. Seven are aliphatic compounds. Thus a trend toward lower quantities of greater than two ring compounds is seen. The list in Table 23 can be added to this, identifying five >2 ring PNA's. As seen in Table 23, and the small peak heights for higher boiling substances in Figure A1, the quantity of >2 ring PNA's is very small.

Figure 18 compares the emissions from the shakeout, before scrubbing, with the MATE value ranges. The values given in the organic extract summary table for sample 1 were inserted into this figure as triangles. Level 1 analysis does not discriminate the subcategories and therefore in a case such as amines, the emission value is safe by an order of magnitude if the amines are primary, but not if they are secondary or aromatic. This table indicates that there may be problems with:

1. Alkyl halides (or Haloaliphatics)
2. Carboxylic acids; derivatives
3. Amines
4. Substituted Benzene Hydrocarbons
5. Fused polycyclics
6. Nitrogen heterocyclics

A closer examination however, remembering that Level 1 analysis seeks only a factor of 3 accuracy, reveals the following:

1. Alkyl halides:

   Of concern only if they are unsaturated. LRMS data indicates a much lower concentration, about 0.03 mg/m^3. Therefore they are not likely a problem.

2. Carboxylic Acids:

   The level only slightly exceeds the MATE for a few members of "Acids with other functional groups". There is no LRMS confirmation. It would be most difficult to propose that a level of concern exists.

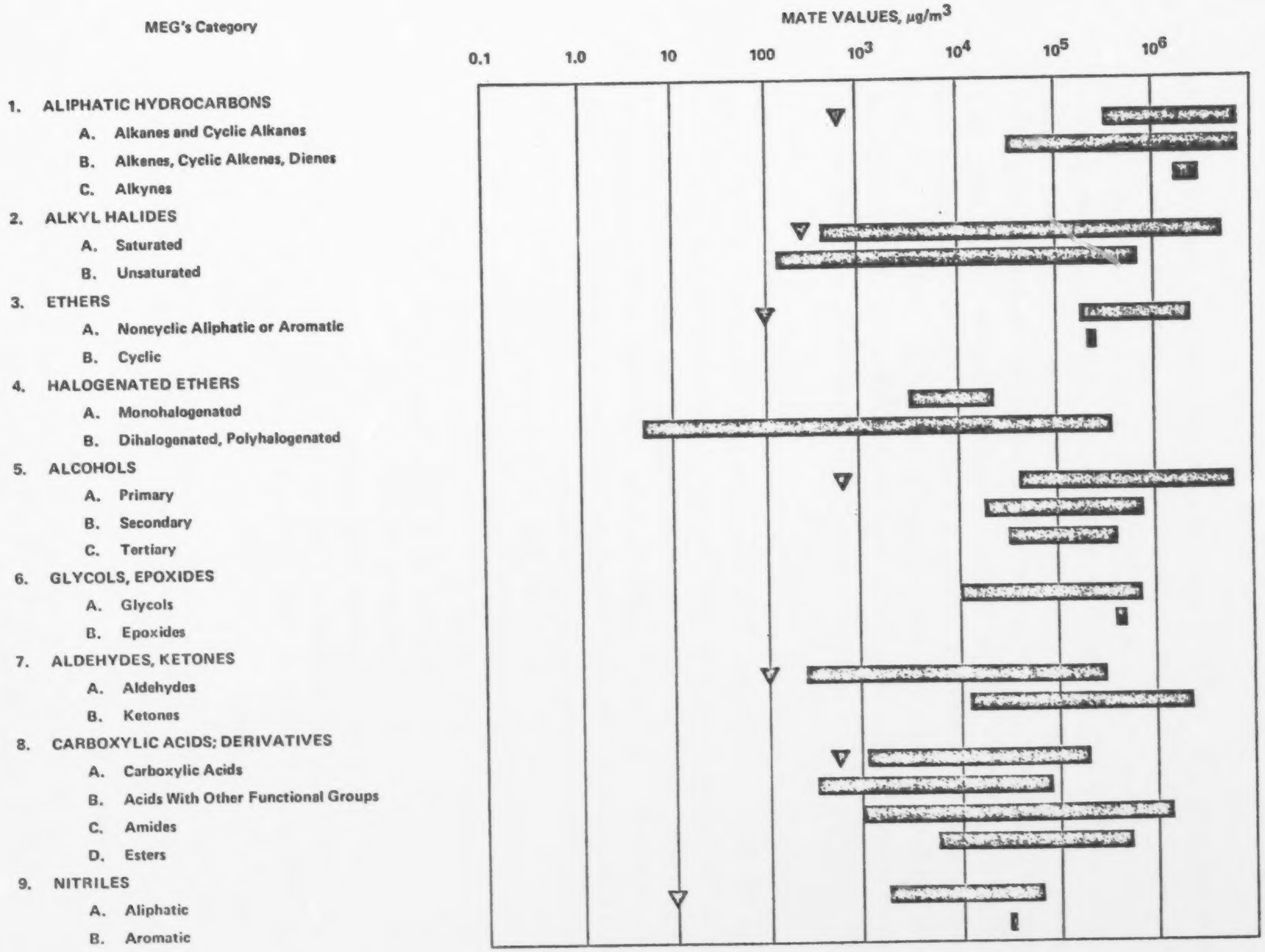

Figure 18. Emissions from shakeout compared with MATEs.

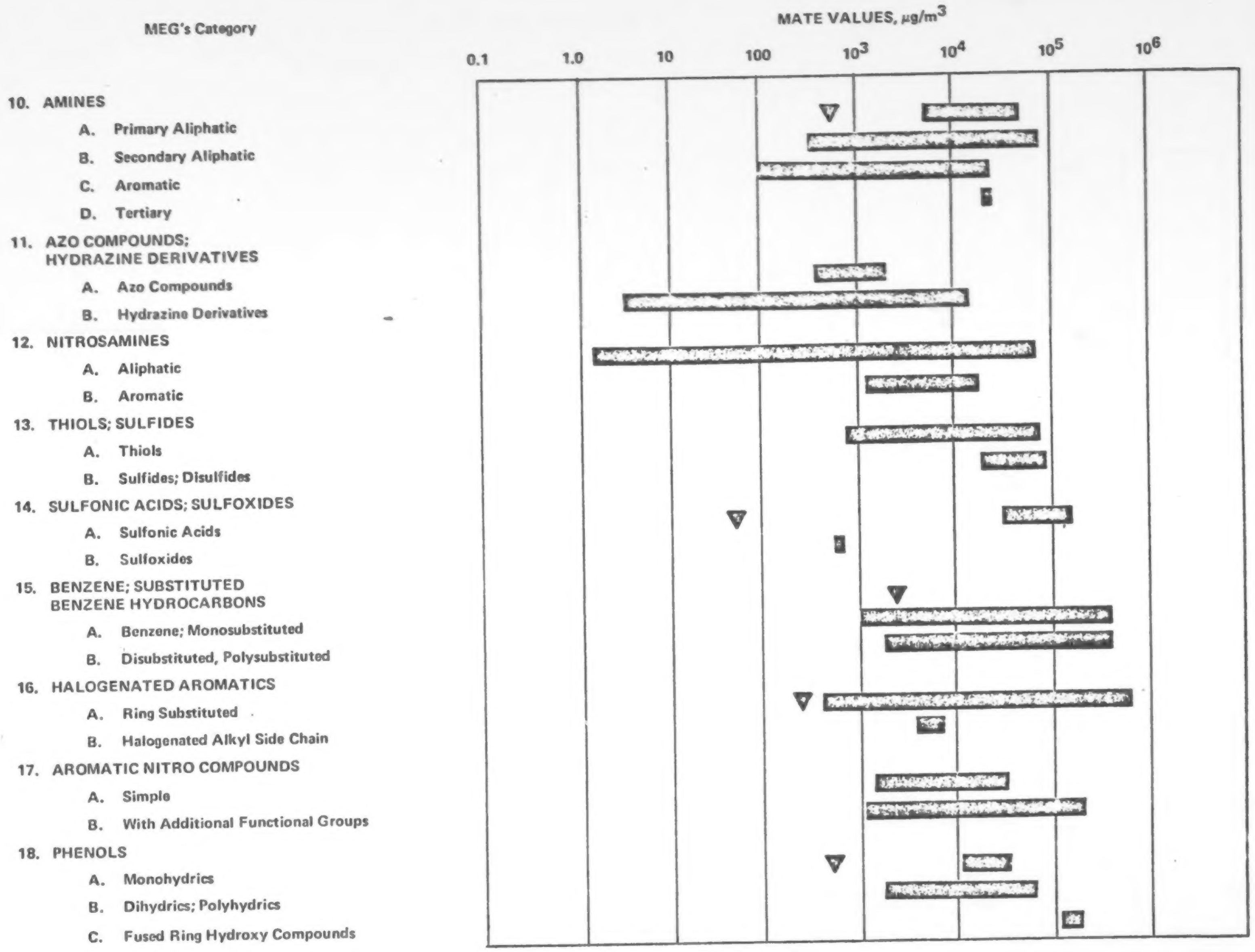

Figure 18. (Continued.)

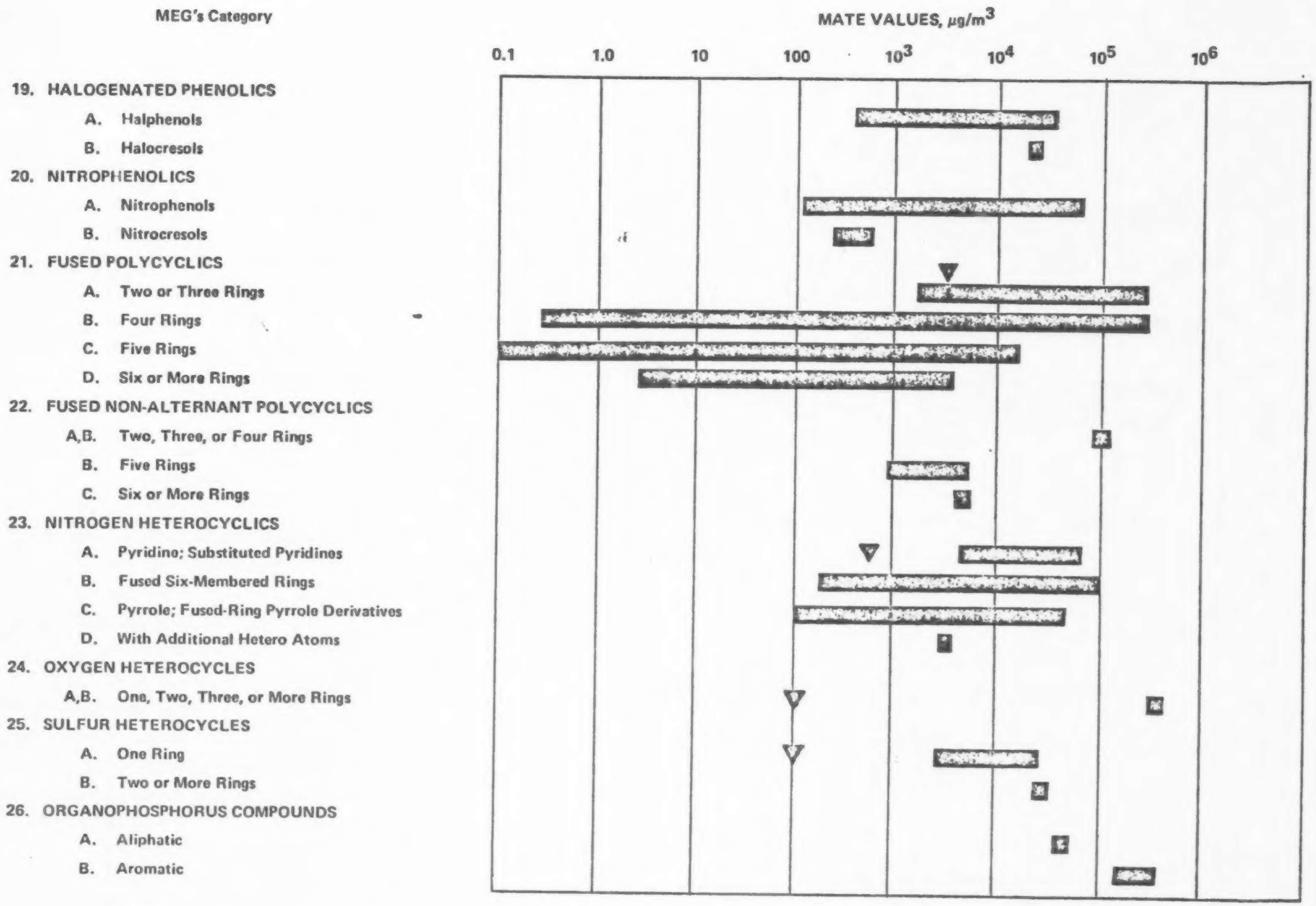

Figure 18. (Continued.)

3. Amines:

No LRMS confirmation. Level exceeds the lowest MATE value by less than an order of magnitude, and then only if they are aromatic amines. It should be noted that aromatic amines are probable in this system and the level of amines is the highest level of concern in the results, with the exception of fused polycyclics.

4. Substituted Benzene Hydrocarbons

This system of pyrolysis products is expected to give the greatest concern in this family of compounds, but the level is less than an order of magnitude above the lowest MATE value.

5. Fused Polycyclics:

Because of the used of seacoal and asphaltic substances, this was the area of greatest concern at the onset of the sampling program. The results indicate very definite problems if the polycyclics are of four or more rings. The GC-MS analysis however did not reveal any concern level in that category but revealed a predominance of naphthalene compounds. The level found is near the lowest MATE values for two ring systems (naphthalene compounds) and is of less concern than amines.

6. Nitrogen Heterocyclics:

Again, these do not show up in the LRMS analysis. The level indicated is less than an order of magnitude above the lowest MATE for pyroles.

In summary, no definitive statement can be made to the effect that the organic emissions are hazardous. There is a possibility that some organic compounds are being emitted above the MATE levels. This is only a reasonable possibility if (a) the entire quantity of family substance found of concern is made up of less than 10 chemical compounds and (b) the compounds present have the lowest MATE values in their category. The probability of both (a) and (b) being true is quite low, certainly less than 10 percent if not less than 1 percent. High resolution studies would show over 1000 chemical compounds, as Bates[21] has indicated, and this factor alone precludes the probability of proposition (a) being true.

8.1.3 Inorganic Analysis

The respirable portion of the particulate (<3μ) was subjected to spark source mass spectrometry. The complete analysis is found in the Appendix. Table 25 presents the portion of the results that indicates a possible

TABLE 25. METAL CONTENT OF <3 MICRON DUST FROM GREEN SAND SHAKEOUT

Element	Observed $\mu g/m^3$	Air MATE $\mu g/m^3$	Concern Ratio (Value/Mate)	Control Level %	Observed µg/g	Land MATE µg/g	Concern Ratio (Value/Mate)	Required Control Level %
Si	12E4**	1E4	12	91.7	18E4	None	-	-
Ca	655	16E3	-	-	9,900	3,200	3.10	67.7
Tr	36.4	6,000	-	-	550	160	3.44	70.9
Cr	73	1	73	98.6	1,100	50	22	95.5
Mn	31.1	5,000	-	-	470	20	23.5	95.8
Fe	1,260	700 to 9,000	1.8 to 0.1	44 to 0	19E3	50	380	99.7*
Ni	26.5	15	1.77	43.4	400	2	200	99.5
Cu	3.8	200	-	-	99	20	4,95	79.8
As	0.79	2	-	-	12	10	1.2	16.7
Se	0.54	200	-	-	<8.2	5	1.64	39
Cd	0.38	10	-	-	5.7	0.2	28.5	96.5
Pb	2.6	150	-	-	40	10	4	75

*Not firmly established yet.

**To economize space, E is used to mean "positive power of 10", thus 1E4 means 1×10^4 or 10,000.

environmental concern. In this, the Air, Health MATE and the Land, ecology MATE values are compared with the sample analysis. A "Concern ratio" was then calculated. This is defined as the ratio of the value found to the MATE value. The concern ratio can be used to determine the degree of control, i.e., the percentage of removal required to reduce the concentration to the MATE value. The Land, ecology values do not apply to the air sample but would apply to the collected dust for landfill considerations. The dominance of Al, Mg, Si in the analysis is consistent with the major composition of the dust being clay and silica.

Of significant concern are Zr, Ba, and the rare earths Ce, Pr, Nd. These are additives to the Mg inoculant. Their appearnce as far down the processing line as the shakeout was not expected. This indicates that the inoculation process should be investigated further.

Since the isocyanate in the binders can conceivably decompose to HCN, a special NaOH bubbler was used on the SASS train to trap cyanides. This analysis is given in Table 26.

TABLE 26. CYANIDE ANALYSIS SAMPLE 1; GREEN SAND SHAKEOUT

Volume NaOH in impinger:	980 ml
CN_- analysis	31.5 ppm
CN_- content	30.87 mg
CN^- load	2.027 mg/m^3
MATE, Air Health, value:	11 mg/m^3
CN^- emissions per ton cast:	6.470 g

8.2 ANALYSIS OF SASS TRAIN SAMPLING OF SCRUBBER EFFLUENT FROM SHAKEOUT OF GREEN SAND MOLDING WITH ISOCYANATE CORES

8.2.1 Total Particulate Loading

Sample 2 was taken from the roof stack after the exit of a wet scrubber of the venturi rod type. The scrubber was 99.54 percent efficient in removing particulates, thus the particulate catch was small. Due to the small catch, the probe and all cyclone catches were rinsed out and combined in the field. The results are presented in Table 27. The summary of Sampling Data is given in Table 28.

8.2.2 Level 1 Organic Analysis

Table 29, the organic analysis summary, gives the LC and IR analysis of vapor phase organics. The detailed LC data is found in the appendix.

TABLE 27. PARTICULATE LOADING, SAMPLE 2, POST SCRUBBER

Category	Weight, mg	Emission concentration mg/m^3	Total emission g/tonne cast
<1μ dust	106.5	4.07	19.8
>1μ dust	126.7	4.85	23.6
(Probe rinse and all cyclone catches were combined in field due to small qty.)			
Total	233.2	8.92	43.4

Sample volume at 15.5° C, dry: 26.15m^3 Total load in grains/ft^3: 0.00390

Metal cast during sample period: 59.81 tones Air flow/tonne cast: 4,865m^3 (std., dry)

TABLE 28. SUMMARY OF SAMPLING DATA FOR SCRUBBER EFFLUENT, SAMPLE NO. 2

Date of test:	6/29/78
Volume of gas sampled:	26.151m^3
Stack gas temperature:	42.77° C
Stack gas pressure:	75.54cm Hg
Stack gass molecular weight:	28.84
Stack gas moisture:	12%
Stack gas velocity:	25.79m/sec.
Stack gas flowrate:	14.375m^3/sec
Total sampling time:	337 minutes
SASS train flowrate:	0.001293m^3/sec
Iron cast during sampling:	72.567 tonnes

As with sample 1, substituted benzenes and fused aromatics predominante. The wet scrubber did little to remove organic vapors.

TABLE 29. SUMMARY OF ORGANIC VAPOR ANALYSIS FROM GREEN SAND SHAKEOUT AFTER WET SCRUBBING, SAMPLE 2

Category	Found mg/m^3	MIN. MATE value in category mg/m^3	Ratio $\frac{\text{conc. found}}{\text{MATE}}$
Aliphatics	0	20	0
Haloaliphatics	0.27	0.1	2.7
Substituted benzenes	2.82	1.0	2.82
Halobenzenes	0.29	0.7	0.4
Fused aromatics	2.82	0.001 to 200	28,000
Hetero N compounds	0.61	0.1	6.1
Hetero O compounds	0.12	300	0.00
Hetero S compounds	0.12	2	0.06
Alkyl S compounds	0.05	1	0.05
Nitriles	0.08	1.8	0.04
Aldehydes, ketones	0.08	0.25	0.32
Nitroaromatics	0.08	1.3	0.06
Ethers, Epoxides	0.08	16	0.01
Alcohols	0.49	10	0.05
Phenols	0.49	2	0.25
Amines	0.49	0.1	4.90
Amides	0.49	1.0	0.49
Esters	0.09	5.0	0.02
Carboxylic acids	0.49	0.3	1.63
Sulfonic acids	0.05	0.8	0.06
TCO	95.17		
GRAV	10.13		

The cyanide emissions were 19 percent less after the scrubber on a per ton cast basis, as indicated in Table 30.

TABLE 30. CYANIDE ANALYSIS, SAMPLE 2

Volume of NaOH in impinger	810 ml
CN$^-$ analysis	38.0 ppm
CN$^-$ content	30.78 mg
CN$^-$ load	1.18 mg/m^3
MATE, Air Health	11 mg/m^3
CN$^-$ emissions per ton cast	5.212 g

8.2.3 Inorganic Analysis

Inorganic analysis an sample 2 was not performed because of the small quantity and the reasonable assumption that the analysis would be essentially the same as that of Sample 1. Since the scrubber is highly efficient (99.5%) for large particulates but not for smaller particulates (25% for <1μ) it is reasonable to assume that the total particulates emitted by the scrubber approximate the <3μ particulates that were analyzed for sample 1.

Applying the analysis of sample 1 to the scrubber emissions reveals the following areas of concern:

Total Scrubber Exhaust Particulates: 8.92 mg/m^3

CR concentration: 1100 μg/g particulate

CR Land, Ecology MATE: 50 μg/g

Cr emission: (8.92 mg/m^3) (1100 ppm) = 9.8 μg/m^3

Cr Air, Health MATE: 1 μg/m^3 (NIOSH recommendation)

TLV: 100 μg/m^3

The data indicate that while chromium is within the Threshold Limiting Value (TLV) by a factor of 10, the Cr in the effluent exceeds the Air Health MATE by a factor of 10 and the land ecology MATE by a factor of 22. Ascertaining the environmental desirability of land filled collected dust will require leachate testing according to the RCRA rules that are presently being formulated and interpreted.

The chromium concentration in the air clearly exceeds NIOSH recommendations, if people are continuously subjected to the undiluted stack effluent.

The source of the chromium could not be ascertained. No chromium bearing clays are used in the foundry tested and no chromium is intentionally added to the metal.

8.3 ANALYSIS OF FUGITIVE EMISSIONS IN THE SHAKEOUT ROOM OF A PHENOLIC SHELL MOLDING FOUNDRY, SAMPLE 3

The pyrolysis products from phenolic molds were considered important enough to analyze (Tables 31 and 32). A well ducted foundry doing this type of work was not located, nevertheless sampling the fugitive emissions was deemed useful. The total particulates and the organic vapors were sampled. These results are presented in the tables that follow. This sample exhibits distinctly different characteristic than the emissions from green sand molding. First it is noted that the TCO and GRAV components are nearly equal. In the previous case of green sand molds the sample was about 94 percent TCO material. TCO material may be adsorbed by the cooler sand surrounding the mold core and could be emitted when the shakeout exposed this sand to the hot metal and hot sand. The higher molecular weight substances are considered to be of greater environmental concern. In the case of shell molding, the shell is thin enough that even the sand on the outside suffers extreme heat.

The iron shot is more permeable than sand and does not present the large surface area for adsorption that clay and sand do. It is therefore reasonable to expect a larger portion of the low boiling volatiles to escape and also burn during the initial period after pouring. These mechanisms would predict a lower yield of TCO material, as was found.

In spite of the differences in sampling conditions, the values for substituted benzenes and fused aromatics are about equal to those in sample 1. A notable difference is the high value of aliphatics, and a nitrile level nearly 50 times that of green sand shakeout.

TABLE 31. SUMMARY OF ORGANIC VAPOR ANALYSIS FROM PHENOLIC SHELL SHAKEOUT, SAMPLE 3

Category	Found mg/m^3	Min. MATE value in category mg/m^3	Ratio $\frac{\text{conc. found}}{\text{MATE}}$
Aliphatics	2.14	20	0.11
Haloaliphatics	0.40	0.1	4.0
Substituted benzenes	2.46	1.0	2.46
Halobenzenes	0.24	0.7	0.34
Fused aromatics	2.46	0.001 to 200	25,000
Hetero N compounds	0.75	0.1	7.5
Hetero O compounds	0.27	300	0.00
Hetero S compounds	0.27	2	0.14
Alkyl S compounds	0.05	1	0.05
Nitriles	0.47	1.8	0.26
Aldehydes, ketones	0.27	0.2	1.35
Nitroaromatics	0.03	1.3	0.02
Ethers, Epoxides	0.27	16	0.02
Alcohols	0.54	10	0.05
Phenols	0.14	2	0.07
Amines	0.54	0.1	5.4
Amides	0.49	1.0	0.49
Esters	0.54	5.0	0.11
Carboxylic acids	0.48	0.3	1.60
Sulfonic acids	0.04	0.8	0.05
GRAV conc.	12.84		
TCO conc.	16.86		

TABLE 32. PARTICULATE LOADING, SAMPLE 3

Category	Weight, mg	Load, mg/m^3
All dust	618.3	49.59
Sample volume at 60° F: 12.47m^3		
Load in grains/ft^3: 0.02167		

8.4 COMPARISON OF ORGANIC EMISSIONS TO MATES

Table 33 lists the major categories of compounds, the values found in samples 1 and 3, and the lowest MATE values for some member of the category. From this it is seen that the only possible problems are with alkyl halides, amines, fused polycyclics, and nitrogen heterocyclics. As stated earlier, the GC-MS results for sample 1 showed that the major carcinogenic members of

TABLE 33. COMPARISON OF ORGANIC EFFLUENTS

Substance Category	Sample 1 mg/m^3	Sample 3 mg/m^3	Lowest MATE for category mg/m^3
Aliphatic hydrocarbons	0.7	2.1	20
Alkyl halides	0.2*	0.4*	0.1
Ethers	0.1	0.3	16
Alcohols	0.6	0.5	10
Aldehydes, ketones	0.1	0.3	0.2
Carboxylic acids	0.5	0.5	0.3
Nitriles	0.01	0.5	1.8
Amines	0.5*	0.5*	0.1
Sulfonic Acids	0.05	0.04	0.8
Substituted Benzenes	2.4	2.5	1
Halogenated Aromatics	0.2	0.2	0.7
Phenols	0.6	0.1	2
Fused polycyclics	2.4*	2.5*	0.0001 to 200
Nitrogen heterocyclics	0.6*	0.8*	0.1

*Possible problem exists.

the fused polycyclics are not present at levels of more than 3 percent of the MATE values and naphthalenic compounds predominate. The fact that similar results were obtained for substituted benzene and fused polycyclics in the case of green sand with seacoal and synthetic asphalt and also in the case of phenol-formaldehyde and sand, indicates that seacoal and heavy organic additives are of no greater concern than any other organic material.

When making the comparisons it must be carefully observed that the values of substance found is the sum of all the members of the category that were present. On the other hand, the MATE values are the lowest value applicable to one member of the category.

With this caveat in view, there is a high probability that the uncontrolled organic emissions from the shakeout do not pose a threat to the environment in foundries that operate in a manner similar to the ones tested.

Evaluating the results from Level 1 testing also requires cognizance of the purpose and philosophy of Level 1 testing. The analytical accuracy expected is only within a factor of three. Thus the true answers could well be less by a factor of three, which would remove most of the categories that reach MATE values. On the other hand the true values could be three times greater than the analytical report. In the present case, this would still result in only the hetero N, amine and fused aromatics exceeding the MATE by a factor of ten. Thus the analytical results do not definitively describe the pollutant level as either unacceptable or safe. To resolve this problem Level 2 testing will be required.

9.0 DISCUSSION OF RESULTS

9.1 ANALYSIS OF PHYSICAL-CHEMICAL MECHANISMS AFFECTING EMISSIONS

A notable result of the testing was the low quantity of high molecular weight compounds in the effluent revealed by the analysis of sample 1, shakeout of green sand with seacoal molds and isocyanate cones. This warrants an explanation since high molecular weight compounds were expected. This will be presented as a mechanistic analysis of the fate of the organic compounds emitted during casting.

Consider a large block of moist sand, clay and high molecular weight organic material, containing a cavity into which iron is poured. The molten iron will heat the sand mixture from the inside toward the outside, producing a high thermal gradient. Figure 10, page 53, shows, by the curves for ½-inch and 1 inch from the sand-metal interface, that the temperature of the sand mixture cannot rise above 212°F (100°C) until after the water content has vaporized. Thus the moisture content helps absorb the heat of the cooling iron and minimizes the distance from the metal-sand interface at which the temperature can rise above 212°F. Since, in addition, dry sand is a good insulator there is a high thermal gradient in the sand surrounding the casting, throughout the cooling period.

The introduction of the molten iron causes the organic material to pyrolyze into lower molecular weight substances. Some of this organic material graphitizes forming the "lustrous carbon" layer next to the metal that produces a good metal finish. The laboratory test of Bates & Scott, found 50% hydrogen, 22% carbon monoxide, 6.4% carbon dioxide, 4.5% methane, and 4.8% higher hydrocarbons in the gases emitted from a sealed mold. The vaporized substances thus formed travel away from the metal-sand interface and into the cooler sand, both by gas pressure and by thermal transpiration.

As the vaporized organic material travels away from the sand-metal interface, it is adsorbed on the clay particles and may condense to a liquid when it encounters sand that is below the boiling point of the substance involved at the partial pressure of the substance. The first action will be adsorption on the clay, since adsorption of a compound onto a solid will occur above its boiling point. This process will be of lower significance relative to the sand, but clay has a very high surface area and can adsorb considerable quantities of material per unit weight. The second action to occur is simple condensation. The permanent gases will, of course, pass on through the sand mixture. Thus, the sand clay mixture will act as a selective trap, adsorbing the higher molecular weight materials (e.g., benzene and larger) more readily than the more volatile materials.

Immediately after pouring iron into a sand mold, gases are observed burning at the seams of the flask and other places that allow escape. The analysis given by Bates & Scott indicates that the majority of burning gases will be hydrogen, carbon monoxide and methane.

Upon shaking out the mold, the cooler sand and clay that have trapped or condensed the hydrocarbons will come into contact with the hot metal and the layer of hot sand surrounding the metal. This will result in vaporizing some of the condensed organics. There are two processes that favor emissions of the lower molecular weight material. The first is the generation stage of pyrolysis, which by its nature breaks larger molecules into smaller molecules, thereby tending to produce more low molecular weight substances.

The second is the revolatization of the condensed hydrocarbons during shakeout. The heating of the cooler sand by the metal and hotter sand is limited, therefore the boiling off of the lower molecular weight and higher vapor pressure compounds will be favored.

If the mold is completely cooled before shakeout, then no secondary boiloff emissions will occur. Thus both the quantity of shakeout emissions and the ratio of the high to low boiling compounds emitted will vary with metal temperature at the time of shakeout. This strongly indicates that cooling time can be used as a technique to control shakeouts emission. Further, foundrymen report that in cases where a casting is cooled overnight, there the emissions on shakeout are nearly completely eliminated.

9.2 COMPARISON OF EMISSIONS FROM DIFFERENT CHEMICAL SOURCES

Two chemical systems were tested:

> Samples 1 & 2: Shakeout of green sand molds containing seacoal and phenolic isocyanate cores.
>
> Sample 3: Shakeout of phenol formaldehyde bound shell molds.

The green sand with seacoal molds were expected to emit substances similar to those emitted by coke ovens and other coal processes. The phenolic shell system was expected to emit the decomposition products of phenol-formaldehyde, especially since the area around the foundry smelled of phenol.

It is reasonable to expect differences in the emissions from these sources, but since Level 1 analysis is by category of compounds, the differences may not appear significant. In addition, Sample 3 was a fugitive sample, thus the concentrations cannot be related to the quantity of casting.

The most obvious difference is in the ratios of high boiling (GRAV material) to low boiling (TCO material) in each sample.

	Sample 1	Sample 2	Sample 3
$\frac{\text{GRAV} \times 100}{(\text{GRAV} + \text{TCO})}$	5.7%	9.6%	43.2%

The differences between samples 1 and 2 are within experimental error but sample 3 exhibits 5.8 times the GRAV material as the average of samples 1 and 2.

In shell molding the shell is about ½-inch thick and is supported in a flask of iron shot. The shell is thin enough for even the outter portions to become very hot. Thus a significant amount of condensation of low boiling compounds on the sand is not expected. There is no moisture in the system to absorb heat and the iron shot has a very low surface area relative to sand or clay, thereby reducing its capacity to trap or condense low boiling organics before they pass through the interticies of the shot and escape in the air of the cooling room. Thus, at the time of shakeout, the proportion of higher boiling compounds in the sand and iron shot is expected to be greater than the low boiling compounds. This explains the experimental results.

Another method of comparing the samples is to examine the quantity of material in each of the LC fractions and express this as the percentage of the total LC material for the sample of concern. This is presented in Table 34, which shows a larger proportion of aromatic hydrocarbons from samples 1 & 2 (Green sand with seacoal and isocyanate cores) than sample 3 (phenol formaldehyde). On the other hand, the phenolic shell molding produced a larger proportion of phenols as seen in fraction 6.

The infrared analysis can be compared for the samples from Tables 22, 29, & 31 by determining the percentage of the total sample for each compound class. This is presented in Table 35, which shows that samples 1 and 2 produced five times the proportion of phenols as sample 3. This discrepency may be caused by the technique of analysis in which the sample extract is applied to a NaCl plate, blown dry, and the IR spectrum measured, thereby losing nearly all TCO material. Samples 1 and 2 were over 90% TCO material, but the Level 1 analysis only identifies functional groups for the 10% of material that did not evaporate. Another difficulty involved is that the procedure requires reading IR spectra of mixtures, which prohibits compound identification and introduces considerable interference. The technique specified is such that a compound with a high extinction coefficient (ability to absorb energy) may be present in small quantities and cause an indication of high concentration while another compound may be present in large

TABLE 34. COMPARISON OF PERCENT OF EACH LIQUID CHROMATOGRAPH FRACTION

LC fraction	Fraction percent			Compound class types*
	Sample 1	Sample 2	Sample 3	
1	16.35	17.66	16.50	Paraffins
2	60.10	60.59	30.30	Aromatic Hydrocarbons
3	8.98	8.45	7.07	Polyaromatic Hydrocarbons
4	0.92	0.76	8.42	Polyaromatic Hydrocarbons
5	1.50	1.14	8.42	Heterocyclic Sulfur Compounds, Esters, Ketones, Alcohols
6	12.09	11.59	28.28	Esters, Ketones, Alcohols, Phenols, Amides, Carboxylic Acids
7	0	0	1.01	Phenols, Amides, Carboxylic Acids, Sulfonates

*Chemical class type found in each fraction.[92]

TABLE 35. PERCENTAGE OF EACH COMPONENT IN SAMPLES (Based on GRAV analysis)*

Category	Sample 1	Sample 2	Sample 3
1. Aliphatics	7.3	0	16.7
2. Haloaliphatics	2.2	2.7	3.1
3. Substituted Benzenes	24.7	28.2	19.1
4. Halobenzenes	2.4	2.9	1.9
5. Fused Aromatics	24.7	28.2	19.1
6. Hetero N Compounds	5.6	6.1	5.8
7. Hetero O Compounds	1.0	1.2	2.1
8. Hetero S Compounds	1.0	1.2	2.1
9. Alkyl S Compounds	0.6	0.5	0.4
10. Nitriles	0.1	0.8	3.7
11. Aldehydes, Ketones	1.0	0.8	2.1
12. Nitro aromatics	0.1	0.8	0.2
13. Ethers, Epoxides	1.0	0.8	2.1
14. Alcohols	5.6	4.9	4.2
15. Phenols	5.6	4.9	1.1
16. Amines	5.6	4.9	4.2
17. Amides	4.7	4.9	3.8
18. Esters	1.5	0.9	4.2
19. Carboxylic Acids	4.6	4.9	3.7
20. Sulfonic Acids	0.5	0.5	0.3
Total Organics, mg/m^3	173.7	105.3	29.7
TCO, mg	2495	2490	210
GRAV, mg	150	265	160
GRAV, mg/m^3	9.85	10.13	12.84
TOC, mg/m^3	163.8	94.17	16.86

*Quantities of substances per cubic meter were used to determine the percentage of each substance in the samples.

concentrations but be read as being present in low concentration due to a low extinction coefficient. Thus the level one procedure is only an approximation, as was intended.

9.3 COMPARISON OF LABORATORY VERSUS FIELD MEASUREMENTS.

In the work of Bates and Scott, emissions from green sand molding were measured by two techniques. In the first, a mold was made in a flask consisting of an iron pipe. After pouring the pipe was capped. Gases produced were vented by a tubulation through a cold trap at 0°C and into a Mylar® bag. The second technique utilized an open mold and a portable sampling hood. After pouring the sampling hood was placed over the mold. This hood provided a known draft and was equipped with a sampling manifold. The gases were drawn from the hood through reagent bubblers and grab samples were also obtained with glass bulbs.

The emission samples were analyzed for cyanide, ammonia, carbon monoxide, carbon dioxide, methane, ethane, ethylene, acetylene, hydrogen and total hydrocarbons. In the hood experiments several compounds were so diluted that they were reported as total hydrocarbons. Ammonia and cyanide were determined with specific ion electrodes and the other compounds were determined by gas cnromatography. Total hydrocarbons were determined by gas chromatography with an unpacked column, and calibrated with methane-air mixtures.

The cold trap condensate contained the higher molecular weight compounds. The organic fraction (about 2%) was separated by silica gel liquid chromatography into three fractions, aliphatic hydrocarbons, aromatic hydrocarbons, and solar compounds. These were analyzed by GC-Mass Spectrometry.

Green sand containing 4-6% clay, 1-2% cereal binder, 3-5% seacoal and other organic additives and 3.5-4% water was used for the tests. The results of the sealed flasks experiments are given in Table 36.[21] The value of total hydrocarbons includes methane, therefore the higher hydrocarbons averaged 4.8%. The volume of gas evolved was 5.5 liters per kg cast thus the emissions of hydrocarbons other than methane was 317 grams per tonne cast.

By comparison, the sampling performed for this assessment found 610 g per tonne for sample 1, green sand shakeout. The greater amount found may

TABLE 36. RANGES OF DECOMPOSITION PRODUCT CONCENTRATIONS IN THE EFFLUENT COLLECTED FROM SEALED FLASK EXPERIMENTS

Compound	Range	Average
Hydrogen	32.0% - 60.0%	50.2%
Carbon Monoxide	16.6% - 23.4%	21.9%
Carbon Dioxide	5.2% - 8.4%	6.4%
Methane	3.9% - 5.5%	4.5%
Total Hydrocarbon	6.8% - 11.3%	9.3%
Ammonia		3 ppm
Cyanide		125 ppm

be the result of a good air flow that enabled a free release of vapors in the shakeout, whereas the sealed flask experiments were limited to those vapors carried out with the steam evolved. The sealed flask experiments can only be compared with pouring emissions in foundry practice.

In the work of Bates and Scott, the heavy organics, obtained from the cold trap, were analyzed by GC-MS. Fourteen polynuclear aromatic and five polar compounds were identified from over 100 GC peaks obtained. No quantitative data was given.

RTI's sampling and analysis identified 16 compounds not identified in Bates & Scott's report, but Bates and Scott identified 14 compounds not identified by RTI's report. In both cases only a fraction of the substances present were identified. RTI specifically quantified the PNA compounds of environmental concern, as given in Table 23. Benzo(a and e)pyrenes and perylene, which were reported by Bates and Scott were not found by RTI. This may be the consequence of the GC column used, and the fact that only one column was used rather than a series of columns. Benzo(a, or e)pyrenes have a molecular weight of 252. RTI did find Chrysene (MW 228) at a concentration of 0.0154 mg/m^3 which is 0.007 of the Air Health Mate value. Since Benzo(a)pyrene has a higher boiling point than chrysene (510° vs 448°C), an argument can be made that a lower concentration would be expected from the shakeout.

The comparison of field tests with laboratory tests involves several difficulties. The best comparison can be made for pouring emissions which can be appropriately simulated in the laboratory. Shakeout emissions will vary in both quantity and quality with the size and shape of castings, time required to remove all sand from the casting, air flow over the return sand belt, and most of all, casting temperature at the time of shakeout. If the casting is cooled to room temperature, then it can safely be predicted that no significant quantities of organic vapor will be evolved.

9.4 RECOMMENDATIONS

The findings of this research indicate the need for further data acquisition and a strong recommendation regarding pollution control from shakeout.

9.4.1 Control of Shakeout Emissions

The test results were explained by a proposed mechanism of emissions. The mechanism presented predicts that shakeout emissions will be reduced with the temperature of the metal at the time of shakeout. This also coincides with observations of industry personnel. Consequently the industry should consider extended cooling time as a method of assisting pollution control and should compare the cost of extended cooling time against the cost of more extensive air pollution control measures that would be required if minimum cooling time is allowed. Such considerations will be affected by the type of casting, quantity and shape of cores, and physical situation of the individual foundry. Estimating the relative cost and merits of cooling as a pollution control measure will require testing to determine emissions as a function of metal temperature. This can be done with "typical types" of castings, and a graph made of emissions versus metal temperature at shakeout. From this the metal temperature required to keep emissions below a target value can be determined. After that, measuring the temperature versus time during the cooling of a specific casting system will identify the cooling time required, and from that the required cooling facilities can be determined.

9.4.2 Pouring Emissions

As indicated previously, the maximum emissions of high molecular weight (>250) substances, such as benzo(a)pyrene and other PNA's should occur at pouring. The degree to which these substances are destroyed by the burning of H_2, CH_3, and CO emissions that occur shortly after pouring is unknown.

When pouring emissions are collected for animal testing, as has been proposed by OSHA, the organization involved could provide samples of the material to EPA which should be subjected to GC-MS and other tests specific for PNA's. If these are found at levels of concern then further research on pouring is indicated. This should start as a laboratory test, possibly implemented by hiring the services of a small foundry, in which a flask is surrounded with a hood, bearing an asbestos board top with a hole for pouring. Provisions should be made to supply nitrogen to the air inlets and to flood the pouring hole with nitrogen. An appropriate fan system will ventilate the hood and provide for sampling with a high volume sampler. Samples of pouring emissions can then be obtained under conditions that do not allow combustion of the emissions. This should be followed with a similar test using air, with gas flames to ignite the pouring emissions. If indeed the unignited emissions have an unacceptably high PNA content, and ignition reduces this to an acceptable value, then the design of flasks to provide ventilation of emissions at holes or tubes that allow deliberate ignition of the gases may be indicated. Under production conditions, the ignition of pouring emissions may or may not be a dependable event. In cases in which it it not a dependable event, special arrangements to force the ignition may provide a substantial reduction in emissions of unacceptable substances.

9.4.3 Inoculation Smoke

As indicated earlier in this report, there is a virtual certainty that inoculation emissions consist of more than MgO. Furthermore, the nature and solubility of the MgO produced is not known. Since inoculation emissions may contain Mg_3N_2 and MgO_2, and definitely must contain oxides of the rare earth additives to the magnesium alloy, collection and characterization of inoculation emissions is indicated.

9.4.4 Chromium Emissions

The high concentration of chromium and nickel in the fine ($<3\mu$) particulates was an unexpected finding. The foundry tries to minimize the level of these elements and does not known what might be their source. This indicates that all further testing of iron and steel foundries should pay careful attention to the metal analysis and an effort to relate the concentration of emitted Cr and Ni to the metal analysis should be made. Laboratory experiments would determine whether or not Cr and Ni are selectively volatilized by reaction with organic materials. If indeed certain organic binders react with Cr and Ni forming volatile metalloorganics or otherwise causing Cr and Ni emissions, then the burden of producing binders that do not enhance these emissions would be upon the chemical binder industry. On the other hand, if seacoal or simply any organic material produces the same result, then the emissions problem must be solved by air pollution control systems. The effect of temperature at the time of shakeout should also be investigated relative to these metals.

A necessary step in future studies of Cr and Ni emissions should be verification of the quantity of these metals "extracted" from the stainless steel SASS train. Published results are needed on the Cr and Ni pick-up by abrasive particulates and any corrosive attack by the chlorinated solvents used for rinsing the system.

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APPENDIX A
DECOMPOSITION PRODUCTS OF SOME SUBSTANCES USED IN MOLDS AND CORES

APPENDIX A
DECOMPOSITION PRODUCTS OF SOME SUBSTANCES USED IN MOLDS AND CORES

Substance	Decomposition Products
INORGANIC-ORGANIC COMPOUNDS:	
Tetraethyl Silicate	At 300°C: formaldehyde silica ethylene 300°C: water and carbon dioxide[31]
Polydimethylsiloxane (silicone)	400°C: formaldehyde silica
Calcium Stearate	A ketone ($C_{17}H_{35}COC_{17}H_{35}$) Carbon dioxide Methane Ethane Ethylene Propylene[32]
Polyphosphate Esters	Phosphine Toluene Benzene Phosphorous pentoxide Carbon dioxide Water Carbon monoxide (in absence of O_2) Potential for highly toxic materials
0,0-diethyl-n,n,-bis (2-hydroxyethyl) aminomethyl phosphonate	Upon burning: 4-ethyl-1-phospha-2,6,7 rioxabicyclo (2,2,2) octane-1-oxide[33] (a toxic organophosphorus compound)

(continued)

Substance	Decomposition Products
ORGANIC MONOMERS:	
Urea	Cyanic acid and ammonia[34]
	At 132°C: biuret which then forms tricyanourea (CN-NH-CO-N(CH)$_2$) or ammonia + cyanic acid
	Ammonium cyanate in absence of water[35]
	Alkyl isocyanates[36]
Thiourea	Ammonia
	Thiocyanic acid
	High temperature, oxidizing conditions: ammonia carbon dioxide sulfur dioxide and/or hydrogen sulfide
	At 140°C in the presence of water: ammonium Thiocyanate
Ammonium Thiocyanate or Thiourea	At 180-190°C: Guanidine thiocyanate
	At 200-300°C: melam carbon disulfide[37]
Pseudocumene	Benzene
	Toluene
	Methane
	Dimerization products such as: 1,3-(3,4-dimethylphenyl) ethane 2,3-4-trimethylphenyl-3,4-dimethylphenyl methane 3,3',4,4'-tetramethyl biphenyl
Ethyl Alcohol	Below 400°C: ethylene methane glycols (e.g., 2-3 butane glycol)

(continued)

Substance	Decomposition Products
Ethyl Alcohol (cont'd)	Above 800°C: ethylene water acetaldehyde then methane and carbon dioxide hydrogen carbon dioxide (in oxidizing conditions)
Stearic Acid	Above 300°C: hydrocarbons (including methane)[40] At 650°C under nitrogen: homologus series of mono-alkenes. Highest is heptadec-1-ene.[41]
Toluenesulfonic Acid	At 400°C: sulfur dioxide substituted phenols (o,m,p cresols) biphenyl derivatives (e.g., 2-methyl biphenyl, 3-methyl biphenyl, 4-methyl biphenyl) possibly toluene[41]
Benzenesulfonic Acid	Sulfur dioxide Substituted phenols Biphenyl derivatives Benzene Distillation yields hydrocarbon and phenyl sulfones[43]
Oleic Acid	Azelaic acid Carbon dioxide Hydrocarbons[44]
Hexamethylenetetramine	Ammonia Formaldehyde Carbon-rich residue[45,46]

(continued)

Substance	Decomposition Products
Hydrol (Tetramethyldiamine-benzhydeol)	No information available
Binaphthyl	Dimers of binaphthyl[47]
ORGANIC POLYMERS:	
Graphite	Oxidizes above 400°C Carbon monoxide
Dextrin	Above 500°C: carbon dioxide carbon monoxide β - blucosan methane ethane ethylene[48]
Waxes (long chain alcohol esters of fatty acids)	Linoleic acid Myristic acid Oleic acid Hexadodecane Dodecene 1,9 - Octodecadiene Ethylene Ethane methane Carbon dioxide[49]
Polyvinyl Alcohol	At 500-800°C: acetaldehyde crotonaldehyde benzaldehyde acetophenone carbon monoxide benzene toluene[50,51]
Furan Resins (furfuryl alcohol resins)	Carbon monoxide and dioxide Ethylene Ethane Propylene

(continued)

Substance	Decomposition Products
Furan Resins (furfuryl alcohol resins) (cont'd)	Propane
	Furan
	Methanol
	Ethanol
	Methane
	Hydrogen and water[52]
Phenol Formaldehyde	At 620°C: carbon monoxide and dioxide hydrogen methane phenol formaldehyde ammonia hydrogen cyanide[53,54] acetylene ethylene ethane[55]
Phenolic Resins (Novalak and Resole)	Same as phenol-formaldehyde plus:
	Allene
	Methylacetylene
	Propylene
	Acetaldehyde
	Methyl chloride
	Acrolein
	Acetone
	Propionaldehyde
	Vinyl chloride
	Ethyl chloride
	Cyclopentadiene
	Benzene
	Methylcyclopentadiene
	Toluene
	Cresols
	Methylenediphenol

(continued)

Substance	Decomposition Products
Phenolic Resins (Novalak and Resole) (cont'd)	C_2 phenols
	Ethylene diphenol
	C_3H_2 phenol Propene[56]
Phenolic-Urethane	Acetylene
	Carbon monoxide and dioxide
	Ethane
	Ethylene
	Hydrogen
	Methane
	The nitrogen in the isocyanate should yield:[57] ammonia simple amines aniline hydrogen cyanide
	The phenolic component should produce: formaldehyde substituted phenols
Alkyd-Urethane	Carbon monoxide and dioxide
	Nitrous oxide
	Hydrogen cyanide
	Benzene
	Toluene
	Methane
	Acetylene
	Hydrogen
	Ethane
	Ethylene
	Ammonia
	Simple amines
	Possibly aniline[57,58]

(continued)

Substance	Decomposition Products
Alkyd-Urethane (cont'd)	Methylene dephenyl isocyanate has been identified in shakeout[58]
Urea-Formaldehyde	At 610°C: carbon monoxide and dioxide hydrogen cyanide methane ammonia nitrogen oxides unidentified substances[55,59]
Polystyrene	At 450°C; benzene toluene ethylene styrene benzaldehyde α-melthyl-styrene phenol methylstyrene n-propyl styrene indene acetophenone methyl indine naphthalene cinnamyl alcohol methyinaphthalene biphenyl or acenaphrhene methylbiphenyl diphenylethane methane ethylbenzene hydrogen[55,60]
Alkyd Resins (mixture of polyfunctional alcohols, dibasic acids, styrene, and filler)	Phthalic anhydride Maleic acid Fumaric acid Ethylene glycol Ethylene Propylene Cyclohexane Carbon dioxide

(continued)

Substance	Decomposition Products
	Methane Products of benzoic acid if it is in the resin.[61]
Wood Flour	Above 400°C: formaldehyde acetone glyoxal formic acid acetic acid lactic acid glycolic acid glycolaldehyde[52] Pyrolysis of lignin produces: acetic acid methanal phenol ethers (e.g., methyl phenyl ether, ethyl phenyl ether, diphenye ether). phenol derivatives (e.g., cresol isomers, ethyl phenols) carbon tars hydrocarbons carbon monoxide and dioxide[62-64]
Pitch	Pyrene Fluoranthene Benzo(a)pyrene Benzo(e)pyrene Benzo(ghi)perylene Anthanthrene Coronene Methane $\leq C_6$ hydrocarbons Benzene 3-Methyl hexane Toluene

(continued)

Substance	Decomposition Products
	3-Ethyl hexane
	3-Methyl heptane
	Nonenes
	Cumene
	Pseudocumene
	Prophenyl benzene
	1-3-Diethyl benzene
	Ethyl-m-xylene
	Amyl benzene
	Hexahydro naphthalene
	Isohexyl benzene
	Napththalene
	Pentamethyl benzene
	1,2,4,5-Tetraethyl benzene
	O-m-Bitoyl
	Acenapthene
	Phenanthrene[65,66]
Linseed Oil	Acrolein
	Myristic acid
	Palmitic acid
	Stearic acid
	Oleic acid
	Linoleic acid
	Linolenic acid
	C_1 to C_{18} hydrocarbons
	Methane (predominant)[67]
	Carbon dioxide
Cereal (corn and wheat flours)	Carbon monoxide and dioxide
	Acetaldehyde
	Acrolein

(continued)

Substance	Decomposition Products
	Acetone
	Butanone
	2-or 3-Methyl furan
	2,3-; 2,4; or 2,5-Demethyl furan
	Acetic acid
	Methyl ethyl or ethyl ethyl furan
	Aliphatic amines (methyl-ethyl-, propyl-, and butyl-amine)
	Phenolics (e.g., cresols, ethyl phenols, xylenols, and dihydroxybiphenyls)[62]
Rosin	1,2-Dimethyl-1,2,3-trans, trans-cyclohexanetricarboxlic acid[69]
(Rosin pitch)	Benzene
	$\leq C_6$ hydrocarbons
	Methylcyclohexene
	2,4-Heptadiene
	Toluene
	1,4-Dimethylocyclohexane
	3-Methylheptane
	2,6-Dimethytheptane
	Xylenes
	Methyloctadiene
	Cumene
	Isopropylcyclohexane
	Ethyltoluene
	Mesitylene
	Isopropyltoluene
	Diethyl benzenes
	Ethyl Xylenes
	3,4-Diethyltoluene
	O-Butyltoluene

(continued)

Substance	Decomposition Products
	Hexahydronaphthalene Pentamethylbenzene Phenylcyclohexane 2-Methylnaphthalene 1,2,4,5-Tetraethyl benzene O,m-Bitolyl Phenanthrene[65]
Kerosene	
alkane components	Low molecular weight hydrocarbons predominantly methane
aromatic components	In low oxygen environment: pyrolyze to dimers dibenzylethane biphenyl[70] alkylbenzene series (i.e., methyl, ethyl, propyl, butyl, amyl substitutions) alkylcyclohexane series (i.e., methyl, ethyl, propyl, butyl, amyl substitutions)[71]
Fuel Oil (C14 to C26 hydrocarbons	Lower hydrocarbons In presence of oxygen: oxygenated derivatives of hydrocarbons, (e.g., acetaldehyde, acetic acid, etc.)[72]
Coal Tars	See products of pitch 1,3-Binaphthylethane if enough O_2 present
(toluene and naphthalene produced form)	Phenyl-1-naphthylmethane[73]
(phenols produced forms)	p-Hydroxy-diphenyl[74]
(fluorene produced forms)	Difluorenylene Rubicene Dihydrorubicene[75]
(n-methylcarbozole content forms)	Phenthridine[76]

(continued)

Substance	Decomposition Products
(anthracene content forms)	Dianthryl[77]
(p-xylene content forms)	p-Dixylyl dimethyl anthracene p,p'-Dimethyl-stilbene[78]
Synthetic Asphalt	Benzene 2,5-Dimethyl-1,5-hexadiene Toluene Octadiene Ethylbenzene Hydrocarbons C_1-C_{22}, C_{24}, C_{25} Styrene Ethyltoluene Misitylene Pseudocumene Butyltoluene Tetrahydronaphthalene α-Hexahydroanthracene Phenanthcene Anthracene Pyrene Fluoranthene Benzo(a) and (e)pyrene Benzo(ghi)perylene Anthanthrene Coronene Carbon monoxide and dioxide Benzene insolubles Quinoline insolubles[66,79]
Gilsonite (one of the purest natural bitumins)	Benzene $\leq C_8$ hydrocarbons C_8 olefins

(continued)

Substance	Decomposition Products
	3,4-Dimethyl hexane
	1,4-Dimethyl cyclohexane
	O-Xylene
	Styrene
	Toluene
	Ethyl benzene
	Propyl benzene
	Ethyl toluene
	Misitylene
	Isobutyl benzene
	Isopropyl toluene
	Diethyl benzene
	Butyl benzene
	Ethyl xylene
	p-Butyl toluene
	1-Methyl anthracene
	Naphthalene
	Penta methyl benzene
	1-Methyl naphthalene
	2-Methyl naphthalene
	1-Ethyl naphthalene
	Diphenylmethane
	Acenaphthene
	m-m'-Bitolyl
	Fluorene
	Stilbene
	Phenanthrene
	Pyrene
	Fluoranthene
	Benzo(a) and (e) pyrene
	Benzo(ghi)perylene

(continued)

Substance	Decomposition Products
	Anthanthrene
	Coronene
	Methane
	Carbon monoxide[65,66]
Petroleum Oil	Lower chain aliphatics
	Lower chain olefins
	Alkyl substituted benzenes
	Products similar to kerosene
	Benzene
	Toluene
	Xylene
	Naphthalene
	Anthracene
	At 750-1000°C: methane (44.8%) hydrogen (20.5%) ethylene (16.2%) propylene (11.9%) other products[80]
Mineral Spirits	Low member hydrocarbons and olefins
Seacoal (finely ground coal)	List approaches 1000. Literature identifies: $\leq C_5$ hydrocarbons hexene benzene trimethyl benzenes 2,3-dimethyl pentane 3-methyl hexane toluene 3-ethyl hexane m- and p-xylene 4-ethly-O-xylene 3-methyl octane pseudocumene phenol indene napththalene 4-ethyl-O-xylene

(continued)

Substance	Decomposition Products
	cresols xylenols dicylo-hexyl 1-ethyl naphthalene 1,4-dimethyl naphthalene acenaphthane 1-naphthol 1,1-binaphthyl fluorene anthracene phenanthrene binaphthyl tetraphenylethane 9-phenylanthracene tetraphenylethylene pyrene fluoranthene benzo(a)pyrene benzo(e)pyrene benzo(ghi)perylene anthanthrene coronene methane carbon dioxide[65,66]
Gluten	Carbon dioxide Acetic acid Aliphatic amines (methyl or ethyl) Phenolics (cresols or ethyl phenols)[36]
Soy Oil	Acrolein Methane Ethane Ethylene Malonic acid Other oxygenated derivatives[32]
Fish Oil	Carbon dioxide Methane series hydrocarbons Olefins (principally ethylene) Unsaturated acids[81]

(continued)

Substance	Decomposition Products
Molasses (sugar content)	Formaldehyde Acetone Glyoxal Glycolaldehyde Glycolic acid Lactic acid Formic acid Acetic acid[82] At 330°C: Furfural 5-methyl furfural carbonyl compounds acids, others[83] At 700°C: H_2O CO_2

APPENDIX B

LEVEL 1 ORGANIC ANALYSIS DATA OF SAMPLES 1-3 AND INORGANIC ANALYSIS DATA

TABLE B-1. STACK DATA, SAMPLES 1 and 2

Properties of Sampling Locations	Stack =1	Stack =2	Stack =3	Stack =4
Purpose of stack	Scrubber Outlet	Duct to Scrubber		
Height ft.	25 ft.	~30 ft.		
Width ft.	3.083 Dia.			
Length ft.	> 25 ft.	> 30 ft.		
Diameter ft., I.D.	3.08 ft.	3.375 ft.		
Wall thickness in.	~1/8 in.	~1/8 in.		
Material of construction	Steel	Steel		
Ports: a. Existing b. Size opening c. Distance from platform	a 3½ in. 3 ft. above roof	a, mode 3½ in. 8 ft. above floor		
Straight distance before port Type of restriction	~ 8 ft.	> 8 ft.		
Straight distance after port Type of restriction	~ 20 ft.	~ 20 ft.		
Environment	Open air on roof	Indoors		
Work space	ample	adequate		
Ambient temperature °F	95-90	90		
Average pitot reading H_2O, in Hg	2.10 in. H_2O	1.81 in. H_2O		
Approximate stack velocity ft/min.	5077	3043		
Approximate std ft^3/min.	30,459	22,304		
Approximate moisture % by volume	12 %	3 %		
Approximate stack temperature °F	109°F	156°F		
Approximate particulate loading gr/SCF				
Approximate particle size				
Approximate composition gases present				
Approximate stack pressure H_2O, in Hg	~30 in Hg	~30 in Hg		
Water sprays	Present in scrubber	Absent		
Used for Sample #	2	1		

TABLE B-2. SASS TRAIN DATA, SAMPLE 1

Company/Location ____

Sampling Location Duct leading from shakeout, Green sand, prescrubber

Run # ____

Date 6-28 Test Participants FJP, BH, EES

Ambient Temp. 90 Bar. Pressure 29.90

Est. Moisture 3 Nozzle (in) 0.497

Pitot Leak Test Good

Sampling Train Leak Test 0.035 - 0.085

Average Δp 0.696

Sampling Point A-3

Start 14:00 Finish 16:50

Clock Time	Dry Gas Meter, Cu.Ft.	Pitot Manometer Δp In.H_2O	ΔH Setting	TEMPERATURE						
				MODULE	IMPINGERS	GAS METER INLET	GAS METER OUTLET	STACK	OVEN	PROBE
0	120.185	0.69	1.69	69	94	109	102	155	220	257
20	194.2	0.69	1.69	69	91	123	109	134	252	250
40	269.6	0.69	1.69	69	87	126	114	144	251	250
60	344.8	0.69	1.86	70	82	126	116	165	252	250
80	422.1	0.69	1.89	61	80	129	118	176	253	250
100	502.9	0.69	1.89	65	78	130	120	147	252	250
120	582.2	0.69	1.89	71	77	132	121	161	251	250
140	661.5	0.69	1.89	64	73	134	122	170	252	250
155	720.605					-				
Diff.	600.420	(=15.23 m^3)								
Average		0.69	1.81	67	83	126	115	156	249	251
	Flowrate= 3.874 cfm = 3.47 dscfm									
	111% isokinetic									

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TABLE B-3. VELOCITY TRAVERSE DATA AND CALCULATIONS, SAMPLE 1

Plant ____________ Location Dust, Shakeout, Green sand, Prescrubber

Date 6-28-78 Time 10:00 Initials FJP

Barometric Pressure 29.90 Moisture Content 3%

Duct Dimensions 40.5" Dia. Pitot Tube Factor .84

POINT NUMBER	DISTANCE IN	ΔP				√ΔP			
		A	B	C	D	A	B	C	D
1	1	0.48	0.56			0.693	0.748		
2	2 3/4	0.69	0.62			0.831	0.787		
3	4 3/4	0.71	0.67			0.843	0.818		
4	7 1/8	0.75	0.68			0.866	0.825		
5	10 1/8	0.81	0.63			0.900	0.794		
6	14 3/8	0.80	0.62			0.894	0.787		
7	26	0.65	0.78			0.806	0.883		
8	30 3/8	0.60	0.84			0.774	0.916		
9	33 3/8	0.61	0.86			0.781	0.927		
10	35 3/4	0.57	0.90			0.755	0.949		
11	37 3/4	0.57	0.94			0.755	0.969		
12	39 5/8	0.57	0.93			0.755	0.964		
sum						9.653	10.367		

Average $\sqrt{\Delta p}$ 0.834 Average Temperature 156 °F

Molecular Weight 28.84 lb/lbmol Duct Area 8.94 ft^2

ENTROPY ENVIRONMENTALISTS, INC.
SPECIALISTS IN SOURCE SAMPLING

Gas Velocity 3043 ft/min

Volumetric Flow Rate 27218 ft^3/min @ stack conditions

Volumetric Flow Rate 22304 ft^3/min @ standard conditions

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TABLE B-4. SASS TRAIN DATA, SAMPLE 2

Company/Location

Sampling Location Scrubber Outlet Stack,
from Green sand shakeout
Date 6-29 Test Participants FJP, BH, EES
Ambient Temp. 90 Bar. Pressure 29.74

Run #

Est. Moisture 12 Nozzle (in) 0.370
Pitot Leak Test Good
Sampling Train Leak Test 0.050 0.080
Average Δp 2.10
Sampling Point A-3
Start 11:27 Finish 17:07

Clock Time	Dry Gas Meter, Cu.Ft.	Pitot Manometer Δp In.H$_2$O	ΔH Setting	Temperature						
				Module	Impingers	Gas Meter		Stack	Oven	Probe
						Inlet	Outlet			
0	724.210	2.10	1.00	67	104	98	97	109	242	256
40	840.500	2.10	1.00	69	86	103	101	110	256	254
80	961.50	2.10	1.00	64	77	109	105	105	254	245
125	092.40	2.10	1.00	75	79	102	105	104	252	255
165	205.80	2.10	1.00	64	71	103	102	109	253	248
200	308.00	2.10	1.00	65	73	107	104	113	253	247
250	457.00	2.10	1.00	63	66	106	106	112	251	253
290	579.90	2.10	1.00	76	66	106	105	112	250	250
330	702.99	2.2	1.00	71	70	104 -	105	108	250	246
337.4	725.035									
	Δ=1000.83 (=26.15m^3)									
Avg.		2.10	1.00	68	77	104	103	109	251	250
	Flowrate =	2.966 cfm								
	78% isokinetic									

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TABLE B-5. VELOCITY TRAVERSE DATA AND CALCULATIONS, SAMPLE 2

Plant ______ Location Scrubber Outlet Stack

Date 6-2-78 Time 10:30 Initials FJP

Barometric Pressure 29.75 Moisture Content 12%

Duct Dimensions 37" dia. Pitot Tube Factor 0.84

POINT NUMBER	DISTANCE IN	ΔP				√ΔP			
		A	B	C	D	A	B	C	D
1	1.6"	203	2.25			1.42	1.50		
2	5.4"	2.70	2.45			1.64	1.56		
3	10.9"	2.15	2.00			1.47	1.41		
4	26.0"	1.70	2.00			1.30	1.41		
5	31.6"	1.75	2.55			1.32	1.50		
6	35.4"	1.65	2.45			1.28	1.56		
7									
8									
9									
10									
11									
12									
sum						8.42	9.04		

Average $\sqrt{\Delta p}$ 1.45 Average Temperature 109 °F

Molecular Weight 28.84 lb/lbmol Duct Area 7.46 ft^2

Entropy Environmentalists, Inc. Specialists in Source Sampling

Gas Velocity 5077 ft/min

Volumetric Flow Rate 37873 ft^3/min @ stack conditions

Volumetric Flow Rate 30459 ft^3/min @ standard conditions

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TABLE B-6. SASS TRAIN DATA, SAMPLE 3

Company/Location Phenolic Shell Molding
Foundry
Sampling Location Shakeout room, fugitive

Date 6-30 Test Participants FJP, BH, TT
Ambient Temp. 95 Bar. Pressure 29.80

Run #

Est. Moisture 3 Nozzle (in) -
Pitot Leak Test -
Sampling Train Leak Test
Average Δp -
Sampling Point -
Start 11:05 Finish 12:52

Clock Time	Dry Gas Meter, Cu.Ft.	Pitot Manometer Δp In.H_2O	ΔH Setting	TEMPERATURE						
				MODULE	IMPINGERS	GAS METER INLET	GAS METER OUTLET	STACK	OVEN	PROBE
0	734.885	-	2.8	65	103	125	103			
15	814.6		2.8	67	92	138	112			
30	886.34		2.8	62	88	135	118			
45	958.10		2.8	64	89	146	125			
60	030.85		2.9	65	82	146 -	129			
75	104.25		3.0	65	76	148	131			
90	177.84		3.0	66	72	149	133			
101	234.905									
						-				
Diff.	500.02	(=12.47 m^3)								
Average			2.87	65	86	140	121			

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TABLE B-7. LC ANALYSIS REPORT, SAMPLE 1

Contractor Research Triangle Institute

Sample Site Duct 5 **Sample Acquisition Date** 28 June 1978

Type of Source Shakeout, Greensand-Isocyanate molding

Test Number 2 **Sample ID Number** 6282-G (XR)

Sample Description Sorbent extract, shakeout, green sand, line 5

Original Sample Volume or Mass 15.23m^3 Std., dry

Responsible Analyst **Date Analyzed**

Calculations and Report Reviewed By **Report Date** 31 August 1978

Column Flow Rate **Column Temperature**

Observations

	TCO mg	GRAV mg	Total mg	Concentration[5] mg/m^3
Total Sample[1]	2495	150	2645	173.7
Taken for LC[2]	74.9	4.5	79.4	5.2
Recovered[3]	78.8	4.1	82.9	5.4

Fraction	TCO[4] in mg			GRAV[4] in mg			Total[4] mg	Concentration[5] mg/m^3
	Total	Blank	Corrected	Total	Blank	Corrected		
1	421	0	421	11	-	11	432	28.4
2	1539	0	1539	66	15	51	1590	104.4
3	209	0	209	51	22	29	238	15.6
4	25	0	25	15	15	0	25	1.7
5	25	0	25	15	0	15	40	2.6
6	276	0	276	66	22	44	320	21.0
7	0	0	0	15	22	0	0	0
Sum			2495			150	2645	173.7

1. Quantity in entire sample, determined before LC
2. Portion of whole sample used for LC, actual mg
3. Quantity recovered from LC column, actual mg
4. Total mg computed back to total sample
5. Total mg divided by total volume

TABLE B-8. ORGANIC EXTRACT SUMMARY

Sample 1. Shakeout, Green Sand, Line 5

	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total Organics, mg/m^3	28.4	104.4	15.6	1.6	2.6	21.0	0	173.7
TCO, mg (94.33 %)	421	1539	209	25	25	276	0	2495
GRAV, mg (5.67%)	11	51.2	29.3	0	14.6	43.9	0	150
GRAV, mg/m^3	0.7	3.4	1.9	0	1.0	2.9	0	9.85

Category	Int/mg/m^3							
Aliphatics	100/0.72							0.72
Haloaliphatics	10/0.07	10/0.15						0.22
Substituted Benzenes		100/1.53	100/0.92					2.45
Halobenzenes		10/0.15	10/0.09					0.24
Fused Aromatics		100/1.53	100/0.92					2.45
Hetero N Compounds					100/0.10	100/0.46		0.56
Hetero O Compounds					100/0.10			0.10
Hetero S Compounds					100/0.10			0.10
Alkyl S Compounds					10/0.01	10/0.05		0.06
Nitriles					10/0.01			0.01
Aldehydes, Ketones					100/0.10			0.10
Nitroaromatics					10/0.01			0.01
Ethers, Epoxides					100/0.10			0.10
Alcohols					100/0.10	100/0.46		0.56
Phenols					100/0.10	100/0.46		0.56
Amines					100/0.10	100/0.46		0.56

TABLE B-8 (cont'd)

Sample 1. Shakeout, Green Sand, Line 5

	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total Organics, mg/m^3								
TCO, mg								
GRAV, mg								

Category	Int/mg/m^3							
Amides					10/0.01	100/0.46		0.47
Esters					100/0.1	10/0.05		0.15
Carboxylic Acids						100/0.46		0.46
Sulfonic Acids						10/0.05		0.05

TABLE B-9. COMPOUND CATEGORIES POSSIBLE IN DIFFERENT LC FRACTIONS (NUMBERS IN PARENTHESIS REFER TO LC FRACTION DESIGNATION)

LC FRACTION 1

Aliphatic Hydrocarbon (1)
Halogenated Aliphatics (1,2)

LC FRACTION 2

Halogenated Aliphatics (1,2)
Monoaromatic Hydrocarbons (2,3)
Halogenated Monoaromatic Hydrocarbons (2,3)
Polyaromatic Hydrocarbon, MW < 216 (2,3)
Polyaromatic Hydrocarbon, MW > 216 (2,3)

LC FRACTION 3

Monoaromatic Hydrocarbons (2,3)
Halogenated Monoaromatic Hydrocarbons (2,3)
Polyaromatic Hydrocarbons, MW < 216 (2,3)
Polyaromatic Hydrocarbons, MW > 216 (2,3)

LC FRACTION 4

Heterocyclic N Compounds (4,6)
Heterocyclic O Compounds (4)
Heterocyclic S Compounds (4)
Nitriles (4)
Ethers and Epoxides (4)
Aldehydes and Ketones (4)
Nitroaromatic Hydrocarbons (4,5)

LC FRACTION 5

Heterocyclic N Compounds (4,6)
Heterocyclic O Compounds (4)
Heterocyclic S Compounds (4)
Alkyl Sulfur Compounds (6)
Nitriles (4)
Aldehydes and Ketones (4)
Ethers and Epoxides (4)
Nitroaromatic Hydrocarbons (4,5)
Alcohols (6)
Phenols (6)
Amines (6)
Amides (6)
Esters (6)

TABLE B-9. (cont'd)

LC FRACTIONS 6 AND 7

- Phenols (6)
- Esters (6)
- Amines (6)
- Heterocyclic N Compounds (4,6)
- Sulfonic Acids and Sulfoxides (7)
- Carboxylic Acids (6,7)
- Alcohols (6)
- Amides (6)

TABLE B-10. IR REPORT--SAMPLE NO. 1, CUT LC-1

Total Sample GRAV = 11.0 mg

ν, cm^{-1}	I	Assignment	Possible Categories	I	Max. Wt. in Total Sample
Quantity Not Sufficient			Aliphatics	100	10.0 mg*
			Haloaliphatics	10	1.0

*Since Aliphatics are consistently shown in this fraction, the total GRAV weight is assigned to that category.

TABLE B-11. IR REPORT--SAMPLE NO. 1, CUT LC-2

Total Sample GRAV = 51.2 mg

ν, cm^{-1}	I	Assignment	Possible Categories	I	Max. Wt. in Total Sample
3030,3053	S	CH, aromatic/ olefinic	Haloaliphatics	10	2.33 mg
2865-2971	S	CH, aliphatic	Substituted Benzenes	100	23.27
1632	W	CH, olefinic	Halobenzenes	10	2.33
1603	S	C=C, aromatic	Fused Aromatics	100	23.27
1509	S	C=C, aromatic			
1445-1456	S	CH, aliphatic			
1308	M	CH, aliphatic			
1034	M	CH, aromatic			
699-875	S	Multiplet			

TABLE B-12. IR REPORT--SAMPLE NO. 1, CUT LC-3

Total Sample GRAV = 29.3 mg

ν, cm^{-1}	I	Assignment	Possible Categories	I	Max. Wt. in Total Sample
3024,3065	S	CH, aromatic	Substitute Benzenes	100	13.95
2871-2971	S	CH, aliphatic	Halobenzenes	10	1.40
1603	S	CH, aromatic	Fused Aromatics	100	13.95
1497	S	CH, aromatic			
1456	S	CH, aliphatic			
1380	W	CH, aliphatic			
1034	W	CH, aromatic			
670-881	S	Multiplet			

TABLE B-13. IR REPORT--SAMPLE NO. 1, CUT LC-4

Total Sample GRAV = 0.0 mg

ν, cm^{-1}	I	Assignment	Possible Categories	I	Max. Wt. in Total Sample
		Quantity Not Sufficient			

TABLE B-14. IR REPORT--SAMPLE NO. 1, CUT LC-5

Total Sample GRAV = 14.6 mg

ν, cm^{-1}	I	Assignment	Possible Categories	I	Max. Wt. in Total Sample
3150,3500	W	OH or NH	Hetero N Compounds	100	1.55
3034,3065	W	CH, aromatic/olefinic	Hetero 0 Compounds	100	1.55
2859,2963	S	CH, aliphatic	Hetero S Compounds	100	1.55
1732	S	C=0, ketone/ester	Alkyl S Compounds	10	0.16
1602	M	NH, amine; CH, aromatic	Nitriles	10	0.16
1495	M	CH, aromatic	Aldehydes, Ketones	100	1.55
1457	S	CH, aliphatic	Nitroaromatics	10	0.16
1276	S	C=0, ester/ether NH, amine	Ethers, epoxides	100	1.55
1221	M	C=0, ester/ether CO, phenol	Alcohols	100	1.55
1028-1124	M	C=0, ether; CO, alcohol	Phenols	100	1.55
701,720	S	CH, substitute	Amines	100	1.55
			Amines	10	0.16
			Esters	100	1.55

TABLE B-15. IR REPORT--SAMPLE NO. 1, CUT LC-6

Total Sample GRAV = 43.9 mg

ν, cm^{-1}	I	Assignment	Possible Categories	I	Max. Wt. in Total Sample
3336	M	OH or NH	Phenols	100	6.97
3028,2065	M	CH, aromatic	Esters	10	0.70
2868-2967	S	CH, aliphatic	Amines	100	6.97
1687	S	C=O, amide/carboxylic acid	Hetero N Compounds	100	6.97
1601	S	C=O, aromatic; NH, amine	Alkyl S Compounds	10	0.70
1508	S	C=O, aromatic	Sulfonic Acids, Sulfoxides	10	0.70
1459	M	CH, aliphatic	Carboxylic Acids	100	6.97
1379	W	CH, aliphatic	Alcohols	100	6.97
1275	S	Amide, carboxylic acid	Amines	100	6.97
1121	M	CH, aromatic			
1028	W	COH, alcohol			
696-812	S	Multiplet			

TABLE B-16. IR REPORT--SAMPLE NO. 1, CUT LC-7

Total Sample GRAV = 0.0 mg

ν, cm^{-1}	I	Assignment	Possible Categories	I	Max. Wt. in Total Sample

Quantity Not Sufficient

TABLE B-17. MASS SPECTROSCOPY REPORT--SAMPLE NO. 1, CUT LC-1

XAD-2 EXTRACT
Total Sample GRAV = 11.0 mg

Quantity Not Sufficient

TABLE B-18. MASS SPECTROSCOPY REPORT--SAMPLE NO. 1, CUT LC-2

XAD-2 EXTRACT
Total Sample GRAV = 51.2 mg

Categories	Relative Intensity
Haloaliphatics	1
Substitute Benzenes	100
Halobenzenes	1
Fused Aromatics (MW <216)	100
Fused Aromatics (MW >216)	100

Possible Identifications	Mol. Wt.	Relative Intensity
Naphthalene	128	10
Phenanthracene, Antharacene	178	100
Pyrene, Fluoranthene	202	100
Chrysene, Benzanthracene	228	10
Benzofluoranthene, Benzopyrene	252	100
Dibenzofluorene	266	10
Indenopyrene, Benzoperylene	276	100

TABLE B-19. MASS SPECTROSCOPY REPORT--SAMPLE NO. 1, CUT LC-3

XAD-2 EXTRACT

Total Sample GRAV = 29.3 mg

Categories	Relative Intensity
Substitute Benzenes	10
Halobenzenes	1
Fused Aromatics (MW <216)	10
Fused Aromatics (MW >216)	100

Possible Identifications	Mol. Wt.	Relative Intensity
Naphthalene	128	10
Phenanthracene, Antharacene	178	10
Pyrene, Fluoranthene	202	10
Chrysene, Benzanthracene	228	100
Benzofluoranthene, Benzopyrene	252	100

TABLE B-20. MASS SPECTROSCOPY REPORT--SAMPLE NO. 1, CUTS LC-4-7

XAD-2 EXTRACT

Sample weight of LC-4 and 7 was Quantity Not Sufficient for analysis.

Mass spectra of LC fractions 5 and 6 were too complex for unequivocal category identification. Assessment of LC-5 and 6 should be based on LC/IR evaluation.

TABLE B-21. METAL CONTENT OF < 3 MICRON DUST, SAMPLE 1 --SHAKEOUT, GREEN SAND

Element	Observed μg/m³	Air Health MATE μg/m³	Observed μg/g	Land Ecology MATE[c] μg/g	MEG Category
Li	0.32	22	4.8	75.	27
Be	0.04	2	0.61	11.	32
B	21.9	3-10E3	330	5000	37
Na	331	2-53E3	5000	N[a]	28
Mg	993	6-10E3	15E3	17E3	33
Al	Major	5-10E3	Major	200	38
Si	12E4	1E4	18E4	N	43
P	21.2	1-10E2	320	(d)	48
S	364	1E3 to 4.4E5	5500	N	53
K	271	2000	4100	4600	29
Ca	655	16E3	9900	3200	34
Ti	36.4	6000	550	160	62
V	0.93	500	14	30	65
Cr	73	1	1100	50	68
Mn	31.1	5000	470	20	71
Fe	1260	700-9000	19E3	50[b]	72
Co	0.79	50	12	50	74
Ni	26.5	15	400	2	76
Cu	3.8	200	58	10	78
Zn	6.6	4000	99	20	81
Ga	1.13	500	17	N	39
Ge	0.07	560	0.99	N	44
As	0.79	2	12	10	49
Se	0.54	200	<8.2	5	54
Br	0.49	1E4	<7.4	N	58
Rb	0.79	12E4	12	N	30
Sr	13.9	3100	210	N	35
Y	0.66	1000	10	N	61
Zr	9.27	5000	140	N	63
Nb	0.86	22E3	13	N	66
Mo	8.61	5000	130	1400	69
Cd	0.38	10	5.7	0.2	82
Sn	0.36	1E4	5.5	N	45
Sb	0.07	500	1.0	40	50
I	0.11	N[a]	1.7	N	59
Cs	0.01	82E3	0.15	N	31
Ba	9.93	500	150	500	36
La	1.9	11E4	28	N	84
Ce	6.62	37E3	100	N	84
Pr	0.31	51E3	4.7	N	84
Nd	1.1	N	17	N	84
Sm	0.19	53E3	2.9	N	84
Dy	0.24	9300	<3.6	N	84
Pb	2.6	150	40	10	46
Th	<0.66	420	10	N	85
U	0.12	9.0	1.8	100	85

[a] N means not determined or not set in the case of MATE values.

[b] The land MATE values are incompletely developed and subject to modification. No MATE value has been set for hydrated ferric oxide, the most probable equilibrium form of iron in the environment.

[c] The land ecology values listed in EPA 600/7-77-136a have been multiplied by 100 to correspond with new recommendations in development.

[d] MATE for elemental P is 0.1 μg/g but this is unsettled as the occurance of elemental phosphorous in the environment will be transitory at best. Phosphate, PO_4^{-3}, is listed as "N" or not determined.

TABLE B-22. LC ANALYSIS REPORT, SAMPLE 2

Contractor Research Triangle Institute

Sample Site Stack 5 **Sample Acquisition Date** 29 June 1978

Type of Source Shakeout, Green sand, post scrubber, line 5

Test Number ______ **Sample ID Number** 6293-G (XR)

Sample Description Sorbent Extract, stack, post scrubber

Original Sample Volume or Mass 26.15 m^3 std., dry

Responsible Analyst ______ **Date Analyzed** ______

Calculations and Report Reviewed By ______ **Report Date** ______

Column Flow Rate ______ **Column Temperature** ______

Observations ______

	TCO mg	GRAV mg	Total mg	Concentration[5] mg/m^3
Total Sample[1]	2490.0	265.0	2755.0	105.4
Taken for LC[2]	74.8	7.9	82.7	3.2
Recovered[3]	81.0	7.2	88.2	3.4

Fraction	TCO[4] in mg			GRAV[4] in mg			Total[4] mg	Concentration[5] mg/m^3
	Total	Blank	Corrected	Total	Blank	Corrected		
1	485.7	0	485.7	0	0	0	485.7	18.6
2	1512.4	0	1512.4	169.3	14.7	154.6	1667.0	63.8
3	224.4	0	224.4	29.4	22.1	7.4	231.8	8.9
4	6.2	0	6.2	29.4	14.7	14.7	20.9	0.80
5	24.6	0	24.6	7.4	0	7.4	32.0	1.2
6	236.7	0	236.7	103.1	22.1	81.0	317.7	12.2
7	0	0	0	22.1	22.1	0	0	0
Sum			2490.0			265.1	2755.1	105.5

1. Quantity in entire sample, determined before LC
2. Portion of whole sample used for LC, actual mg
3. Quantity recovered from LC column, actual mg
4. Total mg computed back to total sample
5. Total mg divided by total volume

TABLE B-23. ORGANIC EXTRACT SUMMARY

Sample 2. Stack, Post Scrubber, Line 5

		LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total Organics, mg/m^3		18.6	63.8	8.9	0.8	1.2	12.2	0	105.3
TCO, mg	90.38%	486	1512	224	6.1	25	237	0	2490
GRAV, mg	9.62%	0.0	154.6	7.4	14.7	7.4	81.0	0	265
GRAV, mg/m^3		0	5.92	0.28	0.56	0.28	3.09	0	10.13

Category	Int/mg/m^3							
Aliphatics								0.0
Haloaliphatics		10/0.27						0.27
Substituted Benzenes		100/2.69	100/0.13					2.82
Halo-enzenes		10/0.27	10/0.02					0.29
Fused Aromatics		100/2.69	100/0.13					2.82
Hetero N Compounds				10/0.08	100/0.04	100/0.49		0.61
Hetero O Compounds				10/0.08	100/0.04			0.12
Hetero S Compounds				10/0.08	100/0.04			0.12
Alkyl S Compounds					10/0.004	10/0.05		0.05
Nitriles				10/0.08	10/0.004			0.08
Aldehydes, Ketones				10/0.08	100/0.04			0.08
Nitroaromatics				10/0.08	10/0.004			0.08
Ethers, Epoxides				10/0.08	100/0.04			0.08

TABLE B-23. (cont'd)

Sample 2. Stack, Post Scrubber, Line 5

	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total Organics, mg/m^3								
TCO, mg								
GRAV, mg								

Category	Int/mg/m^3							
Alcohols					10/0.004	100/0.49		0.49
Phenols					10/0.004	100/0.49		0.49
Amines					10/0.004	100/0.49		0.49
Amides					10/0.004	100/0.49		0.49
Esters					100/0.04	10/0.05		0.09
Carboxylic Acids						100/0.49		0.49
Sulfonic Acids						10/0.05		0.05

TABLE B-24. IR REPORT--SAMPLE NO. 2, CUT LC-1

Sorbent Extract, Stack, Post Scrubber, Line 5

Total Sample GRAV = 0.0 mg

ν, cm^{-1}	I	Assignment	Possible Categories	I	Max. Wt. in Total Sample
Quantity Not Sufficient					

TABLE B-25. IR REPORT--SAMPLE NO. 2, CUT LC-2

Total Sample GRAV = 154.6 mg

ν, cm^{-1}	I	Assignment	Possible Categories	I	Max. Wt. in Total Sample
3024,3053	S	CH, aromatic/ olefinic	Haloaliphatics	10	7.0 mg
2871-2967	S	CH, aliphatic	Substituted Benzenes	100	70.3
1606	M	C=O, aromatic	Halobenzenes	10	7.0
1493	W	C=O, aromatic	Fused Aromatics	100	70.3
1379	M	CH, aliphatic			
1033	M	CH, aromatic			
699-800	S	Multiplet			

TABLE B-26. IR REPORT--SAMPLE NO. 2, CUT LC-3

Total Sample GRAV = 7.4 mg

ν, cm^{-1}	I	Assignment	Possible Categories	I	Max. Wt. in Total Sample
3024	S	CH, aromatic	Substituted Benzenes	100	3.5
2871-2967	S	CH, aliphatic	Halobenzenes	10	0.4
1603	S	C=C, aromatic	Fused Aromatics	100	3.5
1497	M	C=C, aromatic			
1456	S	CH, aliphatic			
1380	W	CH, aliphatic			
1034	W	CH, aromatic			
699-881	S	Multiplet			

TABLE B-27. IR REPORT--SAMPLE NO. 2, CUT LC-4

Total Sample GRAV = 14.7 mg

ν, cm^{-1}	I	Assignment	Possible Categories	I	Max. Wt. in Total Sample
Quantity Not Sufficient			Hetero N Compounds	10	2.1
			Hetero O Compounds	10	2.1
			Hetero S Compounds	10	2.1
			Nitriles	10	2.1
			Ethers, Epoxides	10	2.1
			Aldehydes, Ketones	10	2.1
			Nitroaromatics	10	2.1

TABLE B-28. IR REPORT--SAMPLE NO. 2, CUT LC-5

Total Sample GRAV = 7.4 mg

ν, cm^{-1}	I	Assignment	Possible Categories	I	Max. Wt. in Total Sample
3034	W	CH, aromatic	Hetero N Compounds	100	1.1
2857-2963	S	CH, aliphatic	Hetero O Compounds	100	1.1
1721	S	C=O, ester/ketone	Hetero S Compounds	100	1.1
1603	M	C=O, aromatic	Alkyl S Compounds	10	1.1
1498	M	C=O, aromatic	Nitriles	10	0.1
1456	S	CH, aliphatic	Aldehydes, Ketones	100	1.1
1274	S	COC, ester/ether	Nitroaromatics	10	0.1
1221	M	COC, ester/ether	Ethers, Epoxides	100	1.1
911-1121	M	CH, aromatic	Alcohols	10	0.1
668-750	M	Multiplet	Phenols	10	0.1
			Amides	10	0.1
			Amines	10	0.1
			Esters	100	1.1

TABLE B-29. IR REPORT--SAMPLE NO. 2, CUT LC-6

Total Sample GRAV = 81.2 mg

ν, cm^{-1}	I	Assignment	Possible Categories	I	Max. Wt. in Total Sample
3319	M	NH or OH	Phenols	100	12.9
3035,3070	W	CH, aromatic	Esters	10	1.3
2857-2952	S	CH, aliphatic	Amines	100	12.9
1687	S	C=O, amide/carboxylic acid	Hetero N Compounds	100	12.9
1604	S	C=O, aromatic; NH, amine	Alkyl S Compounds	10	1.3
1509	S	C=O, aromatic	Sulfonic Acids, Sulfoxides	10	1.3
1450	M	CH, aliphatic	Carboxylic Acids	100	12.9
1373	M	CH, aliphatic	Alcohols	100	12.9
1273	S	Amide/carboxylic acid	Amides	100	12.9
1119	W	COH, alcohol; CH, aromatic			
670-818	M	Multiplet			

TABLE B-30. IR REPORT--SAMPLE NO. 2, CUT LC-7

Total Sample GRAV = 0.0 mg

ν, cm^{-1}	I	Assignment	Possible Categories	I	Max. Wt. in Total Sample
		Quantity Not Sufficient			

TABLE B-31. MASS SPECTROSCOPY REPORT--SAMPLE NO. 2, CUT LC-1

Total Sample GRAV = 0.0 mg

Weight of Sample was Quantity Not Suitable for Analysis

TABLE B-32. MASS SPECTROSCOPY REPORT--SAMPLE NO. 2, CUT LC-2

Total Sample GRAV = 154.6

Categories		Relative Intensity
Haloaliphatics		1
Substitute Benzenes		10
Halobenzenes		1
Fused Aromatics (MW <216)		100
Fused Aromatics (MW >216)		100
Possible Identifications	Mol. Wt.	Relative Intensity
Phenanthracene, Antharacene	178	10
Pyrene, Fluoranthene	202	100
Chrysene, Benzanthracene	228	10
Benzofluoranthene, Benzopyrene	252	100
Indenopyrene, Benzoperylene	276	100

TABLE B-33. MASS SPECTROSCOPY REPORT--SAMPLE NO. 2, CUT LC-3

Total Sample GRAV = 7.4 mg

Categories		Relative Intensity
Substitute Benzenes		10
Halobenzenes		1
Fused Aromatics (MW <216)		10
Fused Aromatics (MW >216)		100
Possible Identifications	Mol. Wt.	Relative Intensity
Naphthalene	128	10
Phenanthracene, Anthracene	166	10
Benzofluoranthene, Benzopyrene	252	100
Dibenzofluorene	266	100

TABLE B-34. MASS SPECTROSCOPY REPORT--SAMPLE NO. 2, CUTS LC 4-7

Sample weight of LC-4 and 7 was Quantity Not Sufficient for analysis.

Mass spectra of LC fractions 5 and 6 were too complex for unequivocal category identification. Assessment of LC-5 and 6 should be based on LC/IR evaluation.

TABLE B-35. LC ANALYSIS REPORT, SAMPLE 3

Contractor Research Triangle Institute

Sample Site Shakeout room **Sample Acquisition Date** 30 June 1978

Type of Source Shakeout, phenolic shell molding

Test Number 4 **Sample ID Number** 6304-G (XR)

Sample Description Sorbent extract, Sample 3 Shakeout, phenolic, Line 1

Original Sample Volume or Mass 12.47 m^3 std., dry

Responsible Analyst **Date Analyzed**

Calculations and Report Reviewed By **Report Date**

Column Flow Rate **Column Temperature**

Observations

	TCO mg	GRAV mg	Total mg	Concentration^5 mg/m^3
Total Sample^1	210.0	160.0	370.0	29.7
Taken for LC^2	42.0	32.0	74.0	5.9
Recovered^3	41.4	35.5	76.9	6.2

Fraction	TCO^4 in mg			GRAV^4 in mg			Total^4 mg	Concentration^5 mg/m^3
	Total	Blank	Corrected	Total	Blank	Corrected		
1	32.0	0	32.0	29.3	0	29.3	61.3	4.9
2	59.3	0	59.3	55.0	1.8	53.2	112.5	9.0
3	12.7	0	12.7	16.2	2.7	13.5	26.2	2.1
4	17.2	0	17.2	15.3	1.8	13.5	30.8	2.5
5	23.3	0	23.3	7.2	0	7.2	30.5	2.4
6	65.4	0	65.4	42.4	2.7	39.7	105.1	8.4
7	0	0	0	6.3	2.7	3.6	3.6	0.3
Sum			210			160	370	29.7

1. Quantity in entire sample, determined before LC
2. Portion of whole sample used for LC, actual mg
3. Quantity recovered from LC column, actual mg
4. Total mg computed back to total sample
5. Total mg divided by total volume

TABLE B-36. ORGANIC EXTRACT SUMMARY

Sample 3. Shakeout, Fugitive, Phenolic

		LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total Organics, mg/m^3		4.9	9.0	2.1	2.5	2.5	8.4	0.3	29.7
TCO, mg	(56.76%)	32.0	59.3	12.7	17.2	23.3	65.4	0	210
GRAV, mg	(43.24%)	29.9	53.2	13.5	13.5	7.2	39.7	3.6	160
GRAV, mg/m^3		2.35	4.27	1.08	1.08	0.58	3.18	0.29	12.83

Category	Int/mg/m^3							
Aliphatics	100/2.14							2.14
Haloaliphatics	10/0.21	10/0.19						0.40
Substituted Benzenes		100/1.94	100/0.52					2.46
Halobenzenes		10/0.19	10/0.05					0.24
Fused Aromatics		100/1.94	100/0.52					2.46
Hetero N Compounds				100/0.21	100/0.06	100/0.44	100/0.04	0.75
Hetero O Compounds				100/0.21	100/0.06			0.27
Hetero S Compounds				100/0.21	100/0.06			0.27
Alkyl S Compounds					10/0.01	10/0.04	10/0.00	0.05
Nitriles				10/0.02	10/0.01	100/0.44		0.47
Aldehydes, Ketones				100/0.21	100.0.06			0.27
Nitroaromatics				10/0.02	10/0.01			0.03

TABLE B-36. (cont'd)

Sample 3. Shakeout, Fugitive, Pehnolic

	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total Organics, mg/m^3								
TCO, mg								
GRAV, mg								

Category	Int/mg/m^3							
Ethers, Epoxides				100/0.21	100/0.06			0.27
Alcohols					100/0.06	100/0.44	100/0.04	0.54
Phenols					100/0.06	10/0.04	100/0.04	0.14
Amines					100/0.06	100/0.44	100/0.04	0.54
Amides					10/0.01	100/0.44	100/0.04	0.49
Esters					100/0.06	100/0.44	100/0.04	0.54
Carboxylic Acids						100/0.44	100/0.04	0.48
Sulfonic Acids, Sulfoxides						10/0.04	10/0.00	0.04

TABLE B-37. IR REPORT--SAMPLE NO. 3, CUT LC-1

Total Sample GRAV = 29.3 mg

ν, cm^{-1}	I	Assignment	Possible Categories	I	Max. Wt. in Total Sample
2857-2959	S	CH, aliphatic	Aliphatics	100	26.6 mg*
1464	S	CH, aliphatic	Haloaliphatics	10	2.7
1378	M	CH, aliphatic			
720-971	W				

*Since there is evidence of only one compound category, the total GRAV weight is assigned to that category.

TABLE B-38. IR REPORT--SAMPLE NO. 3, CUT LC-2

Total Sample GRAV = 53.2 mg

ν, cm^{-1}	I	Assignment	Possible Categories	I	Max. Wt. in Total Sample
3031-3052	M	CH, aromatic	Haloaliphatics	10	2.6 mg
2870-2971	S	CH, aliphatic	Substitute Benzenes	100	24.2
1602	M	C=C, aromatic	Halobenzenes	10	2.4
1458	S	C=C, aromatic	Fused Aromatics	100	24.2
1378	M	CH, aliphatic			
698-800	S	Multiplet			

TABLE B-39. IR REPORT--SAMPLE NO. 3, CUT LC-3

Total Sample GRAV = 13.5 mg

ν, cm^{-1}	I	Assignment	Possible Categories	I	Max. Wt. in Total Sample
3030,3056	M	CH, aromatic	Substituted Benzenes	100	6.4 mg
2857-2962	S	CH, aliphatic	Halobenzenes	10	0.6
1740	M	C=O, ketone	Fused aromatics	100	6.4
1604	M	C=O, aromatic			
1494	W	C=C, aromatic			
1457	S	CH, aliphatic			
1378	M	CH, aliphatic			
702-880	S	Multiplet			

TABLE B-40. IR REPORT--SAMPLE NO. 3, CUT LC-4

Total Sample GRAV = 13.5 mg

ν, cm^{-1}.	I	Assignment	Possible Categories	I	Max. Wt. in Total Sample
3000-3100	W	CH, aromatic	Hetero N Compounds	100	2.6 mg
2861-2955	S	CH, aliphatic	Hetero O Compounds	100	2.6
1731	M	Ketone	Hetero S Compounds	100	2.6
1602	M	C=C, aromatic	Nitriles	10	0.3
1466	S	CH, aliphatic	Ether, Epoxides	100	2.6
1378	W	CH, aliphatic	Aldehydes, Ketones	100	2.6
1272	M	COC, ether	Nitroaromatics	10	0.3
1072,1125	W	CH, aromatic; COC, ether			
713,754	M	CH, substituted			

TABLE B-41. IR REPORT--SAMPLE NO. 3, CUT LC-5

Total Sample GRAV = 7.2 mg

ν, cm^{-1}	I	Assignment	Possible Categories	I	Max. Wt. in Total Sample
3444	W	NH or OH	Hetero N Compounds	100	0.8 mg
3038,3057	W	CH, aromatic	Hetero O Compounds	100	0.8
2855-2961	S	CH, aliphatic	Hetero S Compounds	100	0.8
1725	S	C=O, ketone,ester	Alkyl S Compounds	10	0.1
1602	M	C=C, aromatic	Nitriles	10	0.1
1496	W	C=C, aromatic	Aldehydes, Ketones	100	0.8
1454	S	CH, aliphatic	Nitroaromatics	10	0.1
1378	W	CH, aliphatic	Ethers, Epoxides	100	0.8
1278	S	COC, ester/ether	Alcohols	100	0.8
1219	M	COH, phenol; COC, ester	Phenols	100	0.8
1001-1125	M	COH, alcohol; COC, ether	Amines	100	0.8
701,748	M	CH, substituted	Amides	10	0.1
			Esters	100	0.8

TABLE B-42. IR REPORT--SAMPLE NO. 3, CUT LC-6

Total Sample GRAV = 39.7 mg

ν, cm^{-1}	I	Assignment	Possible Categories	I	Max. Wt. in Total Sample
3200-3358	S	NH or OH	Phenols	10	0.5 mg
3067	W	CH, aromatic	Esters	100	5.4
2857-2960	S	CH, aliphatic	Amines	100	5.4
2227	M	C ≡ N, nitrile	Hetero N Compounds	100	5.4
1722	S	Carboxylic acid, ester	Alkyl S Compounds	10	0.5
1659	M	C=O, amide	Sulfonic Acids, Sulfoxides	10	0.5
1608	S	NH, amide; carboxylic acid	Carboxylic Acids	100	5.4
1503	M	C=C, aromatic	Alcohols	100	5.4
1457	S	CH, aliphatic	Amides	100	5.4
1381	M	CH, aliphatic	Nitriles	100	5.4
1273	S	Carboxylic acid, amide; CN, amine			
1115	M	OH, alcohol; CH, aromatic			
718-825	M	Multiplet			

TABLE B-43. IR REPORT--SAMPLE NO. 3, CUT LC-7

Total Sample GRAV = 3.6 mg

ν, cm^{-1}	I	Assignment	Possible Categories	I	Max. Wt. in Total Sample
3000-3400	M	NH or OH	Phenols	100	0.5 mg
2860-2948	S	CH, aliphatic	Esters	100	0.5
1704	S.	Carboxylic acid, ester	Amines	100	0.5
1657	S	C=O, amide	Hetero N Compounds	100	0.5
1605	S	NH, amide; carboxylate	Alkyl S Compounds	10	0.1
1458	S	CH, aliphatic Sulfoxides	Sulfonic acids, Sulfoxides	10	0.1
1399	M	Amide	Carboxylic Acids	100	0.5
1376	M	CH, aliphatic	Alcohols	100	0.5
1258	M	CO, ester; OH, phenol; CH, amine	Amides	100	0.5
1112	S	OH, alcohol			
666,719	M	CH, substituted			

TABLE B-44. MASS SPECTROSCOPY REPORT--SAMPLE NO. 3, CUT LC-1

Total Sample GRAV = 29.3 mg

Categories	Relative Intensity
Aliphatics	100
Haloaliphatics	1

TABLE B-45. MASS SPECTROSCOPY REPORT--SAMPLE NO. 3, CUT LC-2

Total Sample GRAV = 53.2 mg

Categories		Relative Intensity
Haloaliphatics		1
Substituted Benzenes		10
Halobenzenes		1
Fused Aromatics (MW < 216)		100
Fused Aromatics (MW > 216)		100
Possible Identifications	Mol. Wt.	Relative Intensity
Npahthalene	128	10
Acenaphthylene	152	10
Phenanthracene, Anthracene	178	100
Fluoranthene, Pyrene	202	100
Benzanthracene, Chrysene	228	100
Benzofluoranthene, Benzopyrene	252	10

TABLE B-46. MASS SPECTROSCOPY REPORT--SAMPLE NO. 3, CUT LC-3

Total Sample GRAV = 13.5 mg

Categories		Relative Intensity
Substituted Benzenes		10
Halobenzenes		1
Fused Aromatics (MW < 216)		10
Fused Aromatics (MW > 216)		100
Possible Identifications	Mol. Wt.	Relative Intensity
Naphthalene	128	10
Phenanthracene, Antrhacene	178	10
Fluoranthene, Pyrene	202	10
Benzanthracene, Chrysene	228	100
Benzofluoranthene, Benzopyrene	252	10

TABLE B-47. MASS SPECTROSCOPY REPORT--SAMPLE NO. 3, CUTS LC-4-7

Mass spectra of LC fractions 4-6 were too complex for unequivocal category identification. Assessment of LC fractions 4-7 should be based on LC/IR evaluation.